

# EUROPEAN PATENT OFFICE

## Patent Abstracts of Japan

PUBLICATION NUMBER : 09188565  
PUBLICATION DATE : 22-07-97

APPLICATION DATE : 09-01-96  
APPLICATION NUMBER : 08018327

APPLICANT : MARUZEN PETROCHEM CO LTD;

INVENTOR : NISHITANI KATSUTOSHI;

INT.CL. : C04B 35/52 C01B 31/02 C10C 3/04 C10C 3/10

TITLE : POROUS CARBON FORMED BODY HAVING UNIFORM FINE PORE AND PRODUCTION OF THE SAME

ABSTRACT : PROBLEM TO BE SOLVED: To obtain a porous carbon formed body having uniform fine pores by forming a mixture of a specific filler of an infusible substance with a pitch having a high softening point, performing a treatment for making it infusible, burning and carbonizing.

SOLUTION: This porous carbon formed body having uniform fine pores having  $\geq 300^2$  BET specific surface area and  $\leq 10^{-7}$  middle pore diameter, is obtained by first obtaining a pitch having a high softening point (A) having  $\geq 180^\circ\text{C}$  softening point and  $\leq 5\text{wt.}\%$  heat loss at  $\leq 300^\circ\text{C}$  by bringing a formed body obtained by forming a heavy oil having 0.8-1.2 C/H atomic ratio and not containing a portion insoluble to a BTX solvent or a pitch having a low softening point of  $\leq 150^\circ\text{C}$  softening point measured by a temperature gradient method into a particle-like, a powder-like or a fiber-like shape having  $\leq 100\mu\text{m}$  diameter into contact with an organic solvent capable of leaving  $\geq 10\text{wt.}\%$  as an insoluble portion for extracting a light component, then, obtaining an infusible component (B) by performing a treatment to make the component (A) infusible under an atmosphere not containing oxygen, and next, by mixing the component (A) with 20-70wt.% component (B), forming so as to become  $\leq 5\text{mm}$  minimum distance from its center to the outer surface thereof, performing the treatment for making the same infusible under the atmosphere not containing oxygen, burning under an inert atmosphere and carbonizing.

COPYRIGHT: (C)1997,JPO

(19)日本国特許庁(JP)

(12)公開特許公報(A)

(11)特許出願公開番号

特開平9-188565

(43)公開日 平成9年(1997)7月22日

(51)Int.Cl. <sup>8</sup>	識別記号	庁内整理番号	FI	技術表示箇所
C04B 35/52			C04B 35/52	A
C01B 31/02	101		C01B 31/02	101A
C10C 3/04			C10C 3/04	A
				F
3/10			3/10	
審査請求 未請求 請求項の数10 FD (全17頁)				

(21)出願番号 特願平8-18327

(22)出願日 平成8年(1996)1月9日

(71)出願人 000157603

丸善石油化学株式会社

東京都中央区八丁堀2丁目25番10号

(72)発明者 榎谷 正俊

千葉県市原市五井東3丁目10番地15号

(72)発明者 中島 亮一

千葉県市原市山田橋531番地2号

(72)発明者 鈴木 清貴

千葉県袖ヶ浦市川原井2103番地

(72)発明者 重松 等

千葉県市原市大厩1796番地10号

(72)発明者 西谷 勝利

千葉県市原市五井3387番地5号

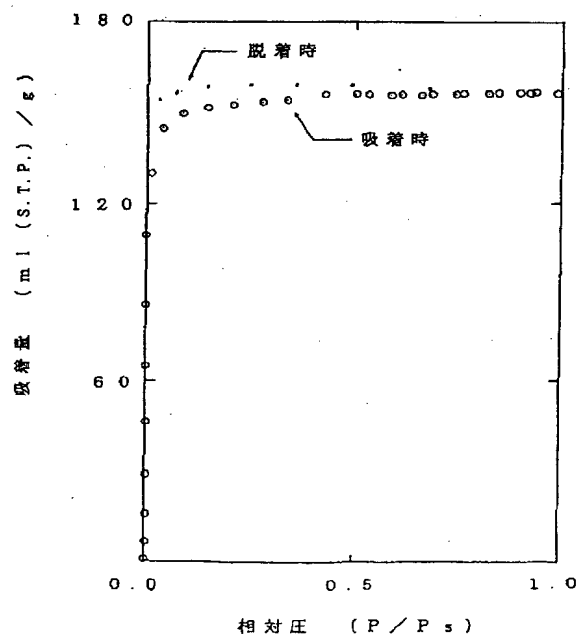
(74)代理人 弁理士 加藤 孝

(54)【発明の名称】 均一微細孔を持つ多孔質炭素成型体およびその製造方法

(57)【要約】

【課題】 均質な炭素で構成された均一微細孔を持つ多孔質炭素成型体、ならびに重質油またはそれから得られる低軟化点ピッチ等の安価な原料を使用し、簡便な手段で上記成型体を得る方法を与える。

【解決手段】 特定性状の重質油またはそれから得られる低軟化点ピッチを原料とし、これを粒子、粉末または繊維状に賦形した後、特定の溶剤で軽質成分を抽出して高軟化点ピッチを得、これを酸素を含む雰囲気下で不融化したものをフィラーとし、不融化処理前の高軟化点ピッチをバインダーとして使用し、フィラーとバインダーとの均一混合物である成型原料を得、これを成型後、酸素を含む雰囲気下で不融化し、さらに不活性雰囲気下で焼成、炭化する。



ベンゼンの吸着脱着等温線(77 K)

## 【特許請求の範囲】

【請求項1】 H/C原子比が0.8~1.2の範囲にある重質油から得られる温度勾配法軟化点が180℃以上、300℃までの加熱減量が5重量%以下であって、BTX溶剤不溶分を実質的に含まない高軟化点ピッチを不融化した不融化物をフィラーとし、H/C原子比が0.8~1.2の範囲にある重質油から得られる温度勾配法軟化点が180℃以上、300℃までの加熱減量が5重量%以下であって、BTX溶剤不溶分を実質的に含まない高軟化点ピッチをバインダーとして使用し、成型して成型体とし、これを不融化、炭化することにより得られる、窒素吸着を用いたBET法による比表面積が300m<sup>2</sup>/g以上であり、かつ、中心細孔径が10Å以下の均質な炭素で構成された均一微細孔を持つ多孔質炭素成型体。

【請求項2】 (出発原料) H/C原子比が0.8~1.2の範囲にあり、BTX溶剤不溶分を実質的に含まない重質油、または該重質油から軽質成分を留去して得られる温度勾配法軟化点が150℃以下であって、BTX溶剤不溶分を実質的に含まない低軟化点ピッチを出発原料とし、

(第1工程) 該出発原料を径100μ以下の粒子状、粉末状または繊維状に賦形して賦形体とする第1工程と、

(第2工程) この賦形体をその少なくとも10重量%は不溶分として残存せしめ得る有機溶剤と接触させることにより軽質成分を抽出し、温度勾配法軟化点が180℃以上で、かつ300℃までの加熱減量が5重量%以下であり、BTX溶剤不溶分を実質的に含まない賦形された高軟化点ピッチとする第2工程と、

(第3工程) この賦形された高軟化点ピッチを、酸素を含む雰囲気中で不融化処理して不融化物フィラーを得る第3工程と、

(第4工程) この不融化物フィラーに、第2工程で得られた高軟化点ピッチと同様にして製造された高軟化点ピッチを、不融化物フィラーと高軟化点ピッチの混合総重量に対する高軟化点ピッチの量が20~70重量%となるように混合した後、必要に応じて粉碎して、高軟化点ピッチをバインダーとする成型原料を得る第4工程と、

(第5工程) この成型原料を成型し、中心部から外表面までの最短距離が5mm以下の成型体を得る第5工程と、

(第6工程) この成型体を、酸素を含む雰囲気中で不融化処理して、フィラー部分、バインダー部分のいずれをも不融化状態とする第6工程と、

(第7工程) この不融化された成型体を不活性雰囲気中で焼成、炭化する第7工程からなることを特徴とする均一微細孔を持つ多孔質炭素成型体の製造方法。

【請求項3】 第6工程の不融化条件が、該不融化物中の酸素濃度が飽和する条件よりも厳しい条件であり、かつ、第7工程の炭化温度が500~1,100℃の温度範囲である請求項2に記載の均一微細孔を持つ多孔質炭

素成型体の製造方法。

【請求項4】 出発原料の重質油がナフサもしくはガスオイルを熱分解してオレフィン類を製造する際に副生する重質油、または石油類を流動接触分解して改質する際に副生する重質油から選ばれた少なくとも1種類の石油系分解重質油である請求項2または3に記載の均一微細孔を持つ多孔質炭素成型体の製造方法。

【請求項5】 第1工程の賦形する方法が、出発原料の粉碎、溶融紡糸またはエマルション化である請求項2ないし4のいずれかに記載の均一微細孔を持つ多孔質炭素成型体の製造方法。

【請求項6】 第2工程の有機溶剤が、パラフィン系炭化水素類、アルコール類、ケトン類、あるいはこれらを混合してなる混合溶剤である請求項2ないし5のいずれかに記載の均一微細孔を持つ多孔質炭素成型体の製造方法。

【請求項7】 該有機溶剤が、n-ペンタン、シクロペンタン、n-ヘキサン、イソヘキサン、シクロヘキサン、n-ヘプタン、イソオクタン、メタノール、エタノール、n-プロパノール、イソプロパノール、n-ブタノール、sec-ブタノール、n-ペンタノール、n-ヘキサノール、シクロヘキサノール、アセトン、メチルエチルケトン、ジエチルケトン、メチルイソプロピルケトンおよびメチルイソブチルケトンから選ばれる少なくとも1種である請求項6に記載の均一微細孔を持つ多孔質炭素成型体の製造方法。

【請求項8】 第1工程の賦形する方法が、エマルション化であり、第2工程の有機溶剤が、アルコール類、ケトン類、あるいはこれらを混合してなる混合溶剤である請求項2ないし4のいずれかに記載の均一微細孔を持つ多孔質炭素成型体の製造方法。

【請求項9】 該有機溶剤が、メタノール、エタノール、n-プロパノール、イソプロパノール、n-ブタノール、sec-ブタノール、n-ペンタノール、n-ヘキサノール、シクロヘキサノール、アセトン、メチルエチルケトン、ジエチルケトン、メチルイソプロピルケトンおよびメチルイソブチルケトンから選ばれる少なくとも1種である請求項8に記載の均一微細孔を持つ多孔質炭素成型体の製造方法。

【請求項10】 均一微細孔を持つ多孔質炭素成型体が、窒素吸着を用いたBET法による比表面積が300m<sup>2</sup>/g以上であり、かつ中心細孔径が10Å以下である請求項2ないし9のいずれかに記載の均一微細孔を持つ多孔質炭素成型体の製造方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は分子吸着剤、触媒、電極炭素等に用いられる均一微細孔を持つ多孔質炭素成型体およびその製造方法に関する。

【0002】

【従来の技術】近年、10Å以下という非常に微細な気孔を持つ炭素材料を、空気中の窒素あるいは炭酸ガスの分離回収に利用する方法が注目されており、圧力差によってガスの吸着脱着を行なうPSA (Pressure Swing Adsorption)法、およびこの用途で使用するMSC (Molecular Sieving Carbon)あるいはCMS (Carbon Molecular Sieve)と呼ばれる多孔質炭素材料の開発が盛んである。

【0003】また、最近、急速に技術、市場が広がっているリチウムイオン電池用負極炭素についても、炭素の細孔構造が電池容量に関係しているとの報告(例えば「炭素の細孔構造と電池性能」1994年炭素材料学会要旨集、p190-191)があり、さらに、電気二重層キャパシターに使用される電極炭素でも微細孔を持つ多孔質炭素が利用されている。

【0004】このように、多孔質炭素材料は従来の吸着剤や触媒以外にも新しい用途への展開が広がりつつあり、さらには粒状、板状またはペレット状等の成型体として使用されるケースも増えてきている。このため、微細な粒子、粉末または繊維状の炭素材料の場合には、炭素材料そのものの細孔構造、細孔分布をコントロールする方法の開発に加えて、多孔質成型体の製造方法の開発も行われている。

【0005】例えば、塩化ビニリデン系共重合体廃棄物を脱塩酸処理した後、粉碎し、これにコールタールピッチ、アスファルト、粘結炭等の焼結剤とアビスル、廃糖蜜、亜硫酸バルブ等の造粒剤を配合して造粒し、不活性雰囲気中で炭化する方法(特開昭50-161485号)、塩化ビニリデン系高分子を脱塩酸処理した後、粉碎し、これに軟化点が50～150℃のピッチとセルロース微結晶集合物、水溶性セルロース誘導体または糖類を配合して造粒し、不活性雰囲気中で炭化する方法(特開昭52-75691号、特開昭52-77017号)、ヤシ殻炭粉末にコールタールまたはコールタールピッチをバインダーとして配合、造粒し、乾留した後、これにクレオソート油を含浸させ、さらに不活性雰囲気中で炭化する方法(特開昭62-176908号)、フェノール樹脂、メラミン樹脂等の粉末にコールタール、ピッチ、クレオソート油等をバインダーとして配合し、造粒した後、不活性雰囲気中で炭化する方法(特開平4-280810号)、高軟化点ピッチを紡糸して繊維状とし、不融化した後に粒状または球状に塊状化し、この塊状物から、ポリビニルアルコール、でんぷん、フェノール樹脂、ピッチ等の溶液または分散液をバインダーとして用いて、塊状物同士を接着した三次元繊維網状体を得、これを不活性雰囲気中で炭化する方法(特開平6-157018号)、高軟化点ピッチを紡糸して繊維状とし、不融化した後、軟化点が80～150℃のピッチ、フェノール樹脂、フラン樹脂等をバインダーとして用いて板状に成型し、不活性雰囲気中で炭化する方法(特開

平7-81915号)等が開示されている。しかしながら、上記の方法では、バインダーまたは粘結剤として用いた有機物が、炭化により必ずしも微細孔を形成するとは限らず、これらの炭化物の気孔生成が少ない場合には成型体全体としての気孔率の低下を招くという問題点がある。このことは、特開平6-157018号、特開平7-81915号にも、バインダー使用量が多くなると「空隙率の低下、および分子ふるい性能の劣化を招いて好ましくない」と記載されていることから明らかである。

【0006】そこで、バインダー部分にも意識的に気孔を持たせようとする方法として、例えば、高軟化点ピッチを紡糸して繊維状とし、不融化した後、軟化点が80～150℃のピッチ、フェノール樹脂、フラン樹脂等をバインダーとして球状不融化繊維塊に成型し、これを再度不融化処理した後に不活性雰囲気中で炭化する方法(特開平6-142503号)、高軟化点ピッチを粉碎して粉末状とし、不融化した後、軟化点が80～150℃のピッチ、フェノール樹脂、フラン樹脂、エポキシ樹脂等をバインダーとして造粒し、これを再度不融化処理した後に不活性雰囲気中で炭化する方法(特開平6-144818号)等が開示されている。しかしながら、このようなバインダーまたは粘結剤を炭化した炭化物が微細孔を形成する方法においても、フィラーである炭素とバインダーまたは粘結剤から生成する炭素とは全く異質なものであり、従って細孔構造が不均一な多孔質炭素成型体とならざるを得ない。

【0007】以上のように、均一微細孔を持つ多孔質炭素成型体の効率的、経済的な製造方法の開発は未だ十分であるとはいえず、さらには、均質な炭素で構成された多孔質炭素成型体およびその製造方法については従来殆ど知られていなかった。

【0008】

【発明が解決しようとする課題】本発明の目的は、均質な炭素で構成され、かつ均一な微細孔を持つ多孔質炭素成型体と、これを工業的に簡便に効率良く、しかも経済的に製造する方法を提供することにある。

【0009】

【課題を解決するための手段】本発明者らは先に、特定の性状を持つ重質油類を出発原料とし、これをまず粒子状、粉末状または繊維状に賦形し、次いでこの賦形体から軽質成分を有機溶剤で抽出除去する方法により得られる高軟化点ピッチを、酸素を含む雰囲気中で酸化して不融化物とし、さらに不活性雰囲気中で炭化処理すると、得られる炭化物は均一微細孔を形成することを見出した(平成7年11月24日出願)。今回、上記目的を達成するため鋭意検討を重ねた結果、さらに、上記の高軟化点ピッチはそれ自体に成型性および自己焼結性を持ち、この高軟化点ピッチの不融化物をフィラーとし、高軟化点ピッチをバインダーとして両者を混合することによ

り、高軟化点ピッチがフィラーの周囲に付着した成型体が容易に得られること、および、この成型体を上記と同様に不融化、炭化処理すると、バインダー部分とフィラー部分が同じ均一な微細孔を形成することを見出し本発明を完成するに至った。

【0010】すなわち、第一の発明の要旨は、H/C原子比が0.8~1.2の範囲にある重質油から得られる温度勾配法軟化点が180℃以上、300℃までの加熱減量が5重量%以下であって、BTX溶剤不溶分を実質的に含まない高軟化点ピッチを不融化した不融化物をフィラーとし、H/C原子比が0.8~1.2の範囲にある重質油から得られる温度勾配法軟化点が180℃以上、300℃までの加熱減量が5重量%以下であって、BTX溶剤不溶分を実質的に含まない高軟化点ピッチをバインダーとして使用し、成型して成型体とし、これを不融化、炭化することにより得られる、窒素吸着を用いたBET法による比表面積が300m<sup>2</sup>/g以上であり、かつ、中心細孔径が10Å以下の均質な炭素で構成された均一微細孔を持つ多孔質炭素成型体に存し、そして第二の発明の要旨は、H/C原子比が0.8~1.2の範囲にあり、BTX溶剤不溶分を実質的に含まない重質油、または該重質油から軽質成分を留去して得られる温度勾配法軟化点が150℃以下であって、BTX溶剤不溶分を実質的に含まない低軟化点ピッチを出発原料とし、該出発原料を径100μ以下の粒子状、粉末状または繊維状に賦形して賦形体とする第1工程と、この賦形体をその少なくとも10重量%は不溶分として残存せしめ得る有機溶剤と接触させることにより軽質成分を抽出し、温度勾配法軟化点が180℃以上で、かつ300℃までの加熱減量が5重量%以下であり、BTX溶剤不溶分を実質的に含まない賦形された高軟化点ピッチとする第2工程と、この賦形された高軟化点ピッチを、酸素を含む雰囲気中で不融化処理して不融化物フィラーを得る第3工程と、この不融化物フィラーに、第2工程で得られた高軟化点ピッチと同様に製造された高軟化点ピッチを、不融化物フィラーと高軟化点ピッチの混合総重量に対する高軟化点ピッチの量が20~70重量%となるように混合した後、必要に応じて粉碎して、高軟化点ピッチをバインダーとする成型原料を得る第4工程と、この成型原料を成型し、中心部から外表面までの最短距離が5mm以下の成型体を得る第5工程と、この成型体を、酸素を含む雰囲気中で不融化処理して、フィラー部分、バインダー部分のいずれをも不融化状態とする第6工程と、この不融化された成型体を不活性雰囲気中で焼成、炭化する第7工程からなることを特徴とする均一微細孔を持つ多孔質炭素成型体の製造方法に存する。

【0011】なお、本発明でいうBTX溶剤とはベンゼン、トルエン、キシレン、エチルベンゼンのような芳香族系溶剤を示す。

【0012】

【発明の実施の形態】以下、本発明についてさらに詳細に説明する。

（出発原料）本発明の出発原料においては、H/C原子比が0.8~1.2の範囲であることが必要である。H/C原子比が0.8より小さいもの、すなわち芳香族性が高く、脂肪族側鎖が非常に少ないものでは、第3工程および第6工程の不融化時に酸素の取り込み速度が遅いため、賦形体および成型体の内部までの十分な不融化、さらには後述するような不融化物中の酸素濃度がほぼ飽和する程度までの過不融化を行おうとする場合には、表面ではすでに酸化消耗が著しく速い状態になり目的物の回収率が下がるので非効率的であり、また酸素の取り込み量が少ない場合には、第7工程の炭化時に成型体内部での溶融が起こったり、また大きな比表面積の生成、すなわち多数の気孔生成が困難になる。逆に、H/C原子比が1.2より大きいもの、すなわち芳香族性が低く、脂肪族性の非常に高いものでは、第2工程の軽質成分の抽出時に回収率が著しく低くなる上、第3工程および第6工程の不融化においても酸素の取り込みよりも分解による脱離が多くなるため、やはり目的物の回収率が低くなる。

【0013】また、出発原料はBTX溶剤に不溶の成分を実質的に含まない、すなわち、JISに規定されているような一般的な不溶分測定法で測定したときの不溶分の値が1重量%以下であることが重要である。これは、BTX溶剤に不溶な成分が存在すると、出発原料をミクロンオーダーの粒子状、粉末状または繊維状に賦形する際の障害になるばかりでなく、これらBTX溶剤に不溶な成分は熱重合等によって生成した分子量の大きい、すなわち縮合芳香族環数の大きい成分であるため、これが多量に含まれていると、不融化時に取り込まれる酸素の量が低下し、ひいては気孔生成の低下、または収率の低下を招くことになる。これは、重質油やピッチ類の不融化では、酸化反応が分子のエッジ部分から起こり内部は酸化され難いため、縮合芳香族環数が大きいと当然分子のエッジ部分に相当する酸素の量は分子全体から見ると小さな値になるからである。

【0014】さらに、本発明の方法では、第1、第2工程を経て得られる高軟化点ピッチをバインダーとして使用するため、出発原料に多量のBTX溶剤不溶分が含まれていると、これから得た高軟化点ピッチも当然BTX溶剤不溶分を含み、このことから、バインダーが均一に混合されない、または不融化物に均一に付着しない等の問題が起こることになる。

【0015】このような本発明の条件を満たす重質油としては、ナフサを分解してオレフィン類を製造する際に副生する重質油（ナフサ分解副生油）、ガスオイル（軽油留分）を分解してオレフィン類を製造する際に副生する重質油（パイロリシスター）、石油類の流動接触分解（FCC）時に副生する重質油（デカント油あるいは

FCCスラリー油)等の石油系分解重質油がある。中でも、ナフサ分解副生油はそもそも原料がナフサであるため、硫黄、窒素、酸素等のヘテロ元素含有量が非常に少なく、炭化時の排ガス処理の面からも好適である。

【0016】なお、コールタールのような石炭系重質油の場合、通常は芳香族性が高くなり(H/Cが小さい)、多量のBTX溶剤不溶分を含むため、そのまま用いることは好ましくないが、BTX溶剤不溶分の分離、除去、あるいは水素化分解等の処理によって本発明の条件に適合するように改質操作を行えば本発明の出発原料として使用可能である。ただしこの場合、改質操作に伴うコストが掛かるので、上記石油系重質油に比較すれば好ましい原料とはいえない。

【0017】本発明の出発原料にはこのような重質油をそのまま使用することもでき、また蒸留操作により軽質成分を除去して得た温度勾配法軟化点が150℃以下の低軟化点ピッチも使用することができる。ここでいう温度勾配法軟化点とは温度勾配のついたアルミ板上に試料ピッチ粉末を置き、これをハケで払い落とし、試料が溶け始めてアルミ板表面に付着する位置を求め、この点のアルミ板の表面温度を軟化点とする方法(測定器:アジア理化工(株)社製、AMK-B2CEFH-3)であり、ピッチの種類、性質によっても異なるが、おおよそ、この温度勾配法軟化点は、JISに規定されたR&B法(リング&ボール法)軟化点よりも15~20℃低い値となり、また、ASTMに規定されたメトラ法軟化点よりも25~50℃低い値となる。

【0018】また、後述する第1工程の方法としてエマルジョン化を採用する場合には、上記の重質油をそのままあるいは必要に応じて粘度調整したもの、また低軟化点ピッチの場合には有機溶剤に溶解して溶液状とすることにより粘度を低くしたものを使用することもできる。このエマルジョン化による方法では、エマルジョン化温度における粘度が1,000ポイズ以下であることが好ましい。この場合、本発明で使用するこれら出発原料はBTX溶剤に不溶の成分を含まないものであるため、溶液とするために用いる有機溶剤にはBTX溶剤が好適であることは言うまでもないが、少なくともこの原料の90重量%以上を溶解することのできる有機溶剤であれば使用可能となる。

【0019】(第1工程)本発明の第1工程は、上記のような特定の原料を径100μ以下の粒子状、粉末状または繊維状に賦形する工程である。

【0020】径を100μ以下にする理由の一つは、次の軽質成分の抽出工程において、抽出が速やかに、かつ均一に起こるようにするためである。径が例えばmmオーダー以上に大きいと、外表面の抽出は速やかに起こるが内部までの抽出に時間がかかるため、抽出時間が不十分であると抽出状態が不均一となる。また一つの理由は、抽出後の不融化工程でも内部まで均一に不融化工態とす

るためである。径が大きい場合、外表面が不融化工態となっても、内部への酸素拡散が遅くなり不均一となる。内部の不融化工態が不十分であるとその後の加熱により溶融、融着を起こしたり、内部まで十分不融化工態しようとすると、表面部分はすでに酸化消耗を起こす状態となり、結果として回収率が著しく低下する。

【0021】賦形の方法は粉碎、紡糸またはエマルジョン化等種々の方法を採用し得る。粉碎による場合、本発明の出発原料は温度勾配法軟化点が150℃以下と低いために、粉碎時に発生する熱によって粒子同士が融着することがあるので、冷却しながら粉碎するか、または多量のガスと混合しながら粉碎することが好ましい。

【0022】また、出発原料の温度勾配法軟化点が室温より十分高い、例えば45℃以上である場合には、紡糸によることもできる。本発明で使用する出発原料はBTX溶剤不溶分を実質的に含まないものであるため、その粘度が数百~数千ポイズとなるように加熱すれば、容易に溶融紡糸が可能である。紡糸の方法はノズルから押し出しこれを牽引して細繊維化する長繊維製造法、ノズルから押し出したピッチを遠心力によって細繊維化する遠心紡糸法、ノズルの直下に高速のガスを流しておきその力で細繊維化するメルトブロー法あるいは渦流法等の方法を採用し得る。紡糸温度は使用する原料の温度勾配法軟化点より50~70℃程高い温度であればよく、従って温度勾配法軟化点が45~150℃の本発明の低軟化点ピッチの紡糸温度は95~220℃の範囲が好ましい。この温度域は不活性ガス中で一般の有機物が分解、変質する温度域より十分低いため、通常の高軟化点ピッチを原料として製造されるピッチ系炭素繊維の紡糸工程で問題となるような紡糸機内での分解、変質、コーキングという現象が起こらず、安定して紡糸をすることができる。なお、温度勾配法軟化点が比較的低い場合には、ノズル孔から出たピッチ繊維が十分冷却されていないと繊維同士が融着する場合があるが、このような場合にはノズル孔から出て、細繊維化されたピッチ繊維を直接第2工程で使用する有機溶剤中に落とすことにより繊維同士の融着を防止することができる。

【0023】さらに、軟化点が45℃より低いかまたは常温で液状の場合は、賦形の方法としてこのような粉碎や紡糸という手段を採用することはできず、エマルジョン化により行う。エマルジョン化の方法については本発明者等は先に特願平6-331132号において開示している。すなわち、「原料重質油類を、1,000ポイズ以下の粘度の液状の状態において、ただし該原料重質油類が当該状態でない場合は、加熱する手段、または水と相溶せず、かつ原料重質油類を90重量%以上溶解する有機溶剤にて希釈ないし溶解する手段、またはこの両手段の併用によって該原料重質油類の状態を当該状態に調製して、剪断力が付与される攪拌方法により界面活性剤の存在下に水と共に攪拌して、該原料重質油類が直径

100 $\mu$ 以下の微細球状粒子として水中に分散されたエマルジョンとする方法」により賦形することができる。

【0024】この方法の特徴は重質油類、ピッチ類を一旦水中でエマルジョン状態とすることであり、エマルジョン状態にある重質油類がその表面張力で球状になることを利用した賦形方法である。なお、上記エマルジョン化には、上記の「剪断力が付与される攪拌」という方法以外に、最近開発された膜乳化法をも採用し得る。この方法は、均一なミクロンオーダーの細孔を持つガラスまたはセラミックスを乳化膜メディアとし、この乳化膜メディアの一方に分散媒である界面活性剤を含む水を入れ循環あるいは攪拌しておき、乳化膜メディアの反対側から分散質である重質油類、ピッチ類、またはピッチを有機溶剤に溶解、希釈した溶液を圧力差により水中に押し出す方法である。押し出される際に分散質は乳化膜メディアの均一な細孔を通過してくるため、その細孔の大きさに比例した粒子として水中に分散され、従って極めて粒子径分布のシャープなエマルジョン粒子を得ることができる。

【0025】以上のようにして、径100 $\mu$ 以下の粒子、粉末または繊維状の賦形体を容易に得ることができる。なお、賦形体の径が小さすぎて、例えば0.1 $\mu$ に満たない微細粒子が多量に含まれるような状態は、後の不融化、炭化時のハンドリングを考えるとむしろ好ましくないが、上記の方法で得られる賦形体の径は、通常は0.1 $\mu$ 以上である。

【0026】(第2工程)本発明の第2工程は、次の不融化工程において支障無く不融化が進行するために必要な性状を有する粒子、粉末または繊維状に賦形された高軟化点ピッチを得る工程である。すなわち、通常、石油系分解重質油から製造されるピッチの空気雰囲気下における酸化開始温度は140～160℃程度であることから、ピッチの軟化点がこの温度より低いと、ピッチの溶解、融着が起これば不融化が困難となる。従って不融化前のピッチの軟化点はこの値より十分高いこと、少なくとも180℃以上、好ましくは200℃以上が必要である。また、ピッチの300℃までの加熱減量が5重量%を越えるようなものでは、不融化工程において同じく溶解、融着の問題が起これば同時に、ピッチから有機物が多量に揮発してくる恐れがあり安全面からも好ましいことではない。従って不融化前のピッチの300℃までの加熱減量は5重量%以下、好ましくは3重量%以下が必要である。

【0027】このような目的で第2工程では、第1工程で賦形されたものから有機溶剤で軽質成分を抽出するが、使用する有機溶剤は出発原料の少なくとも10重量%は不溶分として残存せしめ得るものであることが必要である。これ以上に溶解性の高い有機溶剤を使用すると、得られる高軟化点ピッチの回収率が低下し、効率が悪くなるばかりでなく、第1工程で賦形した形状が崩れ

る場合があるため好ましくない。

【0028】以上の条件を満足する有機溶剤にはパラフィン系炭化水素類、ケトン類またはアルコール類が挙げられる。パラフィン系炭化水素類としては例えば、n-ペンタン、シクロペンタン、n-ヘキサン、イソヘキサン、シクロヘキサン、n-ヘプタン、イソオクタン等、ケトン類としては例えば、アセトン、メチルエチルケトン(MEK)、ジエチルケトン、メチルイソプロピルケトン、メチルイソブチルケトン(MIBK)等、アルコール類としては例えば、メタノール、エタノール、n-プロパノール、イソプロパノール(IPA)、n-ブタノール、sec-ブタノール(SBA)、n-ペンタノール、n-ヘキサノール、シクロヘキサノール等が挙げられ、これらは単独で、または混合して適当な溶解性に調整した混合溶剤として使用される。

【0029】なお、第1工程でエマルジョン化した場合は、水と相溶しない例えばパラフィン系炭化水素溶剤を単独で用いると、スカム状物が生じ分離が困難となるので、この場合には上記有機溶剤の中の水と均一層を形成するアルコール類、ケトン類の使用が好ましい。

【0030】軽質成分の抽出の方法は特に限定されるものではなく、通常知られている方法を採用すればよい。本発明の場合、原料がすでに100 $\mu$ 以下に賦形されているため、例えば賦形された原料を有機溶剤と共に攪拌し、これを濾過、遠心分離して不溶分を回収するという方法で速やかに抽出される。このとき使用する溶剤量は原料の数倍量から数十倍量の範囲で選択すれば良いが、溶剤の使用量が少ないと抽出される量が限定され十分軟化点が高くないことがあったり、賦形された粒子の径が小さい場合には混合後の流動性が悪くなり抽出操作に支障をきたすことがあるため、通常は3～30倍量程度の溶剤を使用することが望ましい。また、抽出時の温度は室温付近で十分であるが、溶解性を高くするため加温することも可能である。抽出時間も特に限定されないが、通常は数時間以下で十分である。また、沸点の高い溶剤を使用した場合、溶剤の除去およびピッチの乾燥には時間がかかるので、この場合には使用した溶剤を濾過等の方法で十分除去した後、その溶剤よりも溶解性が低く、沸点の低い溶剤で洗浄して、沸点の高い溶剤を除いてから乾燥することも好ましい方法である。なお、抽出操作は1回に限定されるものではなく、抽出、分離という操作を繰り返して行っても良い。

【0031】以上のようにして温度勾配法軟化点が180℃以上、好ましくは200℃以上で、かつ300℃までの加熱減量が5重量%以下、好ましくは3重量%以下の高軟化点ピッチを容易に得ることができる。

【0032】本発明の第1工程および第2工程を経て得られる賦形された高軟化点ピッチは、温度勾配法軟化点が180℃以上であり、軟化点という点では炭素繊維用紡糸ピッチと同程度であるにもかかわらず、BTX溶剤

に不溶な成分を含まず加熱減量も少ないという点で炭素繊維用紡糸ピッチと異なっており、このことから、分子量は比較的小さくかつその分布はシャープなものであるということが出来る。また、本発明では従来の高軟化点化後に賦形するという発想から脱却して、先に賦形しその後高軟化点化するという手法を採用しているため、本発明の第1工程、第2工程を通じて従来の高軟化点ピッチの製造において必要であった350℃以上というような高温の加熱処理（熱重合）、あるいは触媒による重合反応を全く使用しないため、経済的に容易に全面光学的に等方性の高軟化点ピッチを得ることが出来る。軟化点が著しく高く、分子量が小さく、かつBTX溶剤不溶分を含まない等方性ピッチという意味では、第2工程で得られるピッチそのものが極めて特異なものであると言うことができ、この特性が後の工程で均一微細孔が容易に、ドラスティックに生成する大きな要因となっていると考えられる。

【0033】（第3工程）本発明の第3工程は、この賦形された高軟化点ピッチを酸素を含む雰囲気下で加熱して酸化し、少なくともその後の加熱で熔融、融着を起こさない程度に不融化された不融化物フィラーを得る工程である。

【0034】本発明の第2工程で得られる賦形された高軟化点ピッチはそもそもBTX溶剤不溶分を含まないものであるが、これを酸素を含む雰囲気、例えば空気中で徐々に加熱すると、140～160℃程度から酸化反応による重量増加が観測されるようになり、それと共にBTX溶剤に不溶な成分およびキノリンに不溶な成分が生成してくる。このとき、BTX溶剤不溶成分が100重量%となっても、キノリン不溶成分がまだ100重量%になっていないものは、後の加熱を伴う工程においてピッチの熔融、融着が発生し、形状変化を起こしたり、気孔の生成に支障をきたす場合がある。本発明者等の知見によれば、後の炭化工程において熔融による形状変化や融着が起こらなくなる点と、不融化物中のキノリン不溶分が100重量%に到達する点がほぼ一致しており、すなわち、熔融も融着も起こさないための不融化に必要な最低条件がほぼこの点に相当し、炭化後の収率もこの点が最も高くなる（以降、この不融化条件を最適不融化条件と言う）。

【0035】従って、第3工程ではBTX溶剤不溶分およびキノリン不溶分が実質的に100重量%に達する条件、すなわち最適不融化条件より厳しい条件で処理すればよい。その不融化方法は酸素を含む雰囲気下で加熱して酸素を取り込ませることができれば特に限定されないが、雰囲気中の酸素濃度によって当然処理条件は異なり、例えば空気雰囲気下の場合には、昇温速度0.1～10℃/min、保持温度250～400℃、保持時間0.1～10時間程度が採用される。

【0036】以上の条件をもって処理すれば、後の加熱

で熔融、融着を起こさない程度に不融化された粒子、粉末または繊維状の不融化物フィラーを得ることが出来る。

【0037】なお、本発明の目的物である成型体とはせずに、粒子、粉末または繊維をそのまま多孔質炭素材料とする場合には、この第3工程で得られる不融化物をそのまま後述する第7工程と同様の条件下で焼成、炭化するか、もしくは後述する過不融化処理を行ない過不融化物とした後に焼成、炭化すればよいが、これらの処理を行なった過不融化物ならびに炭化物を本発明のフィラーとして使用することも可能であることはいうまでもない。ただし、不融化物を使用した場合でも、過不融化物または炭化物を使用した場合でも、成型体を第6工程で過不融化状態とすれば気孔の生成状況には大きな差異はないため、エネルギーコスト的には不融化物を使用することが有利である。

【0038】（第4工程）本発明の第4工程は、この不融化物フィラーに、本発明の第2工程までと同様にして得られた高軟化点ピッチをバインダーとして、不融化物フィラーと高軟化点ピッチの混合総重量に対する高軟化点ピッチの量が20～70重量%となるように配合し成型原料を得る工程である。

【0039】配合の方法は、不融化物フィラーに高軟化点ピッチを混合し、この混合物にBTX溶剤を添加して高軟化点ピッチを溶解、混練した後、この溶剤を含む混合物からBTX溶剤を除去、乾燥する方法、または、高軟化点ピッチをあらかじめBTX溶剤に溶解して溶液としたものを不融化物フィラーに添加、混練し、この溶剤を含む混合物からBTX溶剤を除去、乾燥する方法により実施するのが好ましい。

【0040】不融化物フィラーと高軟化点ピッチを乾式で混合することもできるが、両者共径が100μ以下という微細な粉末状であるため、フィラーの周囲に十分バインダーを付着させることが難しく、混合が不均一な場合、成型体のムラが生じ、その後の加熱でクラックや変形が発生することがあるため十分な注意が必要である。一方、BTX溶剤を用いて高軟化点ピッチを溶解し混合すれば、混合は極めて容易であり、これを乾燥してBTX溶剤を除くことで、不融化物フィラーの周囲にバインダーである高軟化点ピッチが付着した成型原料を容易に得ることが出来る。

【0041】BTX溶剤による高軟化点ピッチの溶解、フィラーとバインダーの混合、BTX溶剤の除去、乾燥のための設備はいずれも市販の混合機、乾燥機等を採用すれば良く、特別な設備や装置は必要ではない。

【0042】また、高軟化点ピッチを溶解するために添加されるBTX溶剤の量は、高軟化点ピッチ1重量部に対して0.3～10重量部が好ましい。この量よりBTX溶剤が少ないと、高軟化点ピッチのBTX溶剤溶液の粘度が高くなり、混合時に大きな機械力が必要であった



り、混合が不均一となる場合がある。逆に、BTX溶剤が多すぎても、フィラーがバインダー溶液中に沈降した状態となるため混合が不均一となったり、また、BTX溶剤の除去、乾燥時に多量の熱エネルギーを必要とするため好ましくない。

【0043】不融化物フィラーに配合する高軟化点ピッチの量は、不融化物フィラーと高軟化点ピッチの混合総重量の20～70重量%、好ましくは30～60重量%である。高軟化点ピッチの配合量が20重量%より少ないと、成型後および不融、炭化後の強度が低くなるため、取り扱い時の破壊等の問題が起こることがあり好ましくない。逆に、高軟化点ピッチの配合量が70重量%よりも多いと成型体の不融時に内部が溶融、膨張し成型体に変形することがあるためやはり好ましくない。

【0044】なお、高軟化点ピッチの配合量、BTX溶剤の使用量、さらには混合、混練機、乾燥機の種類等によつては、混合物に一部塊状部分ができることがあるが、これらは成型時の金型への充填操作や充填物の均一性の障害になることがあるため、成型前にこれらの塊状部分を粉碎、解砕しておくことが好ましい。

【0045】(第5工程) 本発明の第5工程は、第4工程で得られた成型原料を成型し、径または厚さが10mm以下のペレット状、粒状、または板状等の成型体を得る工程である。成型の方法は、加圧成型法、またはBTX溶剤を添加しながら造粒した後に乾燥する方法、もしくは押し出し成型等が採用できる。

【0046】加圧成型による場合、本発明の第4工程で得られた成型原料はフィラーの周囲にバインダーが付着したものであるため、そのまま加圧することで容易に成型体とすることができる。成型の方法は通常知られている方法を採用すればよく、たとえば、径が10mm以下の金型に所定量の成型原料を入れ、ピストンまたはパンチで加圧する方法が採用される。この時の成型圧力は、0.1～数t/cm<sup>2</sup>程度であるが、フィラーの周囲には十分バインダーが付着しているため、それほど大きな圧力は必要とせず、1.0t/cm<sup>2</sup>以下で十分である。また、成型時の温度は常温付近でよい。加熱することもあるが、バインダーの軟化点は180℃以上であるため、この軟化点より低い温度ではバインダーを流動化させることはできず、あまり効果はない。

【0047】また、金型を使わず造粒法によつて粒状物を得ることも可能である。本発明の場合、バインダーである高軟化点ピッチがBTX溶剤に可溶であるため、BTX溶剤を造粒用液体として用いることができ、たとえば、不融化物フィラーと高軟化点ピッチを回転パン型造粒機に入れ、これを回転しながらBTX溶剤を徐々に加えるという方法により粒状化できる。この方法では高軟化点ピッチが、造粒操作中には造粒用バインダーとして作用し、得られた粒状物を乾燥してBTX溶剤を除いた場合には粒状物のバインダーとして、さらには、不融

化、炭化時のバインダーとして作用するため、特に別の造粒用バインダーを用いる必要はない。さらに、不融化物フィラーと高軟化点ピッチにBTX溶剤を加えてペースト状とし、押し出し成型法により成型することも可能である。なお、これらBTX溶剤を使用して成型する造粒法または押し出し成型法の場合には、本発明の第4工程と第5工程とを同時に行うこともできる。

【0048】また、この第5工程で得られる成型体の径または厚さは10mm以下であること、すなわち成型体の中心部から外表面までの最短距離は5mm以下であることが必要である。成型体の径または厚さがこれより大きいと、次の成型体の不融工程において成型体内部までの不融が困難となり、内部が十分不融化されていないと、炭化時に溶融、変形が起こったり、内部に気孔が生成しない部分が残ったり、気孔の不均一な成型体となるため好ましくない。これら、粒状物の粒子の大きさや強度は用いる高軟化点ピッチの配合量と、BTX溶剤の使用量を選択することにより調整可能である。

【0049】(第6工程) 本発明の第6工程は、第5工程で得られた成型体を酸素を含む雰囲気中で不融化処理して、フィラー部分およびバインダー部分のいずれをも不融化状態、好ましくは過不融化状態とする工程である。

【0050】一般に、強度に注目して製造されるピッチ系炭素繊維の不融化条件は、不融化物中のBTX溶剤不溶分およびキノリン不溶分が実質的に100重量%に達する条件、すなわち第3工程で記載した最適不融化条件が好ましいといわれている。しかしながら、本発明の場合、最適不融化条件による不融化物を次の第7工程で炭化すると、炭化温度が600～800℃という狭い温度範囲ではある程度大きな比表面積を有する炭化物が得られるが、これよりも炭化温度が低い場合や逆に高い場合には、得られる炭化物の比表面積が急激に小さくなる。一方、最適不融化条件よりも過酷な条件で処理した場合、すなわち、最適不融化条件では不融化物中の酸素濃度がまだ増加途中であるが、最適不融化条件よりも高温、長時間の条件を採用し過不融化すると、不融化物の収率は徐々に低下するものの、ある条件以上では不融化物中の酸素濃度がほぼ一定になる。この酸素濃度が飽和した状態の過不融化物を炭化した場合には、500℃以上から、取り込まれた酸素が脱離するとともに多数の気孔が生成し、炭化物は十分大きな比表面積を有するようになり、この比表面積は1,100℃という高温まで維持されるようになる。

【0051】従つて、広い炭化温度範囲で十分大きな比表面積を持つ成型体を得るには、この第6工程では、単に最適不融化条件で不融化するよりも、BTX溶剤不溶分およびキノリン不溶分が実質的に100重量%に達するよりも厳しく、かつ、該処理物中の酸素濃度が飽和する以上の条件で処理し、フィラー部分およびバインダー

部分のいずれをも過不融化石態とすることが好ましい。

【0052】この不融化石の方法は特に限定されるものではなく、操作上は本発明の第3工程において高軟化点ビッチの賦形体を不融化石とする際に採用される条件とはほぼ同じ範囲、すなわち空気雰囲気下、昇温速度0.1～10℃/min、保持温度250～400℃、保持時間0.1～10時間程度が採用され、この際、過不融化石態とするには、保持温度や保持時間を調節することにより実施できる。

【0053】また、本発明の第6工程を経て得られる不融化石あるいは過不融化石成型体の比表面積は、処理条件の如何にかかわらず、粒子、粉末または繊維の外表面積に相当する面積しか観測されない。このことは、この不融化石段階で気孔が生成しているわけではないことを示している。

【0054】(第7工程)本発明の第7工程は、第6工程で不融化石された成型体を不活性雰囲気中で焼成し、炭化する工程である。

【0055】炭化方法は不活性雰囲気中で加熱するという通常の方法で良いが、炭化温度は前記の通り第6工程における不融化石条件によって異なり、最適不融化石条件で不融化石した場合の炭化温度は600～800℃、最適不融化石条件以上で十分に過不融化石した場合の炭化温度は500～1,100℃の範囲が選択される。本発明の方法ではこの温度範囲の時に大きな比表面積、すなわち多量の微細孔が得られる。

【0056】例えば、ナフサ分解副生油を出発原料として第1～6工程を経て得られた過不融化石の成型体を窒素雰囲気中、10℃/minで昇温し、所定温度で1時間保持する方法により炭化したものについて、液体窒素温度での窒素吸着によるBET法比表面積を測定してみると、炭化温度400℃では小さな比表面積しか観測されないが、温度をわずか100℃高くして500℃とすると非常に大きな比表面積が観測されるようになる。また、炭化温度1,100℃ではやはり大きな比表面積が観測されるが、さらにわずか100℃高い1,200℃で炭化すると小さな比表面積しか観測されなくなる。また、酸素濃度が飽和していない不融化石を炭化した場合でも、同様に、炭化温度600～800℃の範囲において大きな比表面積が観測される。すなわち、本発明の方法では気孔の生成、消滅がきわめてドラスティックであり、炭化条件のわずかな変化で比表面積が大きく変化する。このことは、本発明の多孔質炭素成型体中の気孔が極めて均一であることを裏付けるものであると考えられる。

【0057】なお、本発明でいう気孔の生成、消滅とは、液体窒素温度で窒素の吸着が起こるかどうかによって判定するものであり、窒素分子が入り込めないような極めて微細な気孔の存在を否定するものではない。例えば、上記の炭化温度による比表面積のドラスティックな

変化は、炭化温度を1,100℃から1,200℃へと高くした時、1,100℃で存在していた“窒素分子が入り込めるような気孔”のほとんどが、一挙に“窒素分子が入り込めないような極めて微細な気孔”に変化した結果であると解釈することもできる。

【0058】本発明の第7工程における炭化温度以外の他の条件、すなわち昇温速度、保持時間等は通常用いられる範囲で十分である。ただし、一般的に知られているように、昇温速度は使用する炭化炉の形式によって実現できる範囲が異なるため、バッチ式の炭化炉を使用する場合には1℃/min～100℃/min程度が、また連続式の炭化炉を使用する場合には10℃/min～1,000℃/min程度の昇温速度が採用され、保持時間は1分～10時間程度が採用される。

【0059】本発明の方法で得られる多孔質炭素成型体は液体窒素温度下の窒素吸着によるBET法比表面積が300m<sup>2</sup>/g以上であり、窒素の吸着等温線からHK法(Horvath-Kawazoe法)で解析した細孔径はその殆どが10Å以下に集中している。

【0060】なお、本発明の方法で生成する気孔のように微細な分子サイズの気孔についてはまだ細孔径、細孔分布、細孔容積を正確に測定する方法が確立されておらず、測定の方法、解析の手法等によってその値が相当大きく変わる場合が多い。従って、分子サイズレベルの気孔の評価はそれぞれの用途毎に実用特性を評価すべきであるが、現実には通常窒素(分子サイズ、長径=4.1Å、短径=3.0Å、特開平4-13288号に記載された値)等の吸着特性から特定解析手法に従って気孔を評価する方法が採用されており、材料の基本特性、あるいは製造法や条件による基本特性の変化等を知る上ではこうした評価方法で十分であると考えられている。

【0061】以上のような方法と条件を採用して本発明の方法を実施すれば、均質な炭素で構成され、かつ、均一な微細孔を持つ多孔質炭素成型体を容易に効率よく製造することができる。

【0062】また、本発明の方法によれば、全く気孔の存在しない炭素材料またはその成型体をも製造することが可能であり、この意味では本発明は均一微細孔の生成を意図的にコントロールする一つの“ポロシティーコントロール法”を提供するものであると言うこともできる。

【0063】

【実施例】以下、参考例、実施例、比較例によりさらに詳細に本発明を説明するが、本発明の範囲はこれらの実施例によって限定されるものではない。なお、参考例、実施例、比較例中の%は特に指定がない限り重量%を示す。

【0064】参考例1

ナフサを分解してオレフィン類を製造する際に副生する重質油(ナフサ分解副生油)を減圧蒸留して温度勾配法

軟化点71℃の低軟化点ピッチを得た。このもののナフサ分解副生油に対する収率は73%であった。またこのピッチの性状はキシレン不溶分0%、キノリン不溶分0%、熱天秤で測定した300℃までの加熱減量17.9%、元素分析値はC92.9%、H7.0%、S0.02%、H/C原子比0.90であった。

【0065】このピッチを径(D)0.25mm、長さ(L)0.75mm(L/D比=3)のノズルを装着した溶融紡糸機に入れ、紡糸温度135℃、吐出圧力5Kg/cm<sup>2</sup>・Gで吐出し、ノズル下部に設置したエアーサッカーで引き取り、繊維径20μmの低軟化点ピッチ繊維を得た。

【0066】次にこの低軟化点ピッチ繊維200gをアセトンとSBAの混合溶剤(アセトン/SBA容量比=20/80)4,000mlの中に入れマグネティックスターラーで1時間攪拌した。その後、この混合物をG-4ガラスフィルターで濾過して溶剤可溶分を除き、得られた不溶分を再度新しい混合溶剤4,000mlの中に入れて1時間攪拌した。これを同じガラスフィルターで濾過し、メタノールで3回洗浄した後、固形物を減圧乾燥機に入れ、30℃で5時間乾燥し、軽質成分を除去した高軟化点ピッチを得た。

【0067】得られた高軟化点ピッチの収率は低軟化点ピッチ繊維に対して58%であり、その性状は温度勾配法軟化点216℃、キシレン不溶分0%、キノリン不溶分0%、300℃までの加熱減量2.1%、元素分析値はC92.8%、H7.1%、S0.03%、H/C原子比0.91であった。このものを走査型電子顕微鏡(SEM)で観察したところ、繊維径は抽出前とほぼ同じであるが、長さが数十μmに切断された繊維状粉末であった。

【0068】ついで、この高軟化点ピッチ繊維の粉末を空气中、昇温速度0.5℃/minで加熱し、195~355℃の所定温度で1時間保持することにより不融化处理し、さらにこの不融化物を窒素気流中、昇温速度10℃/minで加熱し、1,000℃で1時間保持することにより炭化した。不融化物の収率と性状ならびに炭化物の収率と外観を表1に示す。なお、収率は軽質成分抽出後の高軟化点ピッチ繊維を基準とした。

【0069】表1より不融温度215℃以下のものでは炭化時に溶融して繊維形状を維持できず、また、不融温度235℃の場合は繊維形状はとどめているものの繊維同士が融着を起こし塊状になるので、繊維が融着することなく炭化できる最低の不融温度は255℃であり、繊維強度を目的とする場合にはこの条件が最適不融条件となることがわかる。

【0070】また、不融化物の性状変化を見ると、最適不融条件の時に丁度キノリン不溶分が100%に到達しているが、酸素濃度はまだ増加の途中であり、不融温度300℃程度まで増加し、300℃以上ではほぼ飽和

することがわかる。

【0071】次に、得られた炭化物について直読式表面積測定装置、MONOSORB(MS-8型、QUANTACHROME社製)を用い、ASTM法(Draft Proposal 7-18-76, Revision 2 4-6-81)に従って液体窒素温度における窒素吸着量からBET法比表面積(SA(BET))を測定した。その結果も表1に示す。同表から、最適不融条件(255℃)では非常に小さな比表面積しか観測されず、窒素が吸着するような気孔は殆ど存在しないが、不融温度を高くして過不融状態にしたもの、すなわち不融化物中の酸素濃度がほぼ飽和する条件(295℃)以上では大きな比表面積が観測され、微細な気孔が生成していることがわかる。

【0072】また、不融温度255℃および355℃で得た炭化物について、吸着等温線測定装置BELSORP-28SA型(日本ベル(株)製)を用いて液体窒素温度での吸着等温線を測定し、このデータからLangmuir法による比表面積(SA(Lang))を求めた。その結果を表1に合わせて示す。吸着等温線から求めた比表面積は不融温度255℃ではやはり1m<sup>2</sup>/g以下であり、窒素が吸着するような気孔は生成していないことが再確認された。また、不融温度355℃のものでは688m<sup>2</sup>/gという大きな値が確認された。

【0073】これらのLangmuir法による比表面積の値はMONOSORBを用いたBET法とは異なる値となったが、微細な気孔の比表面積測定の場合、測定法の違い、比表面積の計算を行う際に使用する理論計算式の違いが得られる値に大きく影響することは周知のことである。本発明の効果を検証するにはいずれの方法でも良いと判断されたが、実施例では主にBET法により測定し、部分的にLangmuir法により測定した。

【0074】なお、上記のような炭化処理をする前の不融化物の比表面積は、いずれの不融条件を採用したときも0.2~0.4m<sup>2</sup>/g程度であり、これは繊維径と長さから計算される外表面積とほぼ同等の値であった。従って不融化時点では気孔は生成していなかったと考えられる。

【0075】また、不融温度を355℃として得た炭化物の液体窒素温度における窒素の吸着脱着等温線を図1に示す。同図から、絶対圧(P/Ps、P:測定温度における窒素の吸着平衡圧、Ps:測定温度における窒素の飽和蒸気圧)が非常に小さい領域で殆どの吸着が起こっていること、すなわち同炭化物には分布のシャープな非常に微細な気孔が存在することがわかる。なお、図1では吸着時の等温線(丸)と脱着時の等温線(点)に若干のヒステリシスが認められる。このようなヒステリシスは非常に微細な気孔の測定においてしばしば観測されるものであり、その原因については明確にされていないが、このことが均一微細孔の生成を否定するものではない。

【0076】また、このデータからHK法(Horvath-Kawazoe法)に従って細孔分布を計算したところ、この炭素材料の気孔は中心細孔径が約6Åであり、シャープな

分布をした均一微細孔であることが確認された。

【0077】

【表1】

表1

不融化温度 ℃	不融化物の収率と性状						炭化物の収率と性状			
	収率 wt%	不溶分 wt%		元素分析値 wt%			収率 wt%	外観	比表面積 m <sup>2</sup> /g	
		キシレン	メタノール	C	H	O			SA (BET)	SA (Lang)
195	103	69	0	86.7	6.2	7.1	—	炭化時に溶解	—	—
215	103	100	33	—	—	—	—	炭化時に溶解	—	—
235	102	100	75	78.4	4.5	17.1	63	繊維同士が融着	0.2	—
255	100	100	100	—	—	—	64	良好	0.3	0.4
275	96	100	100	71.2	3.1	25.7	60	良好	5.8	—
295	91	—	—	—	—	—	56	良好	320	—
315	90	—	—	69.5	2.3	28.2	53	良好	368	—
335	82	—	—	—	—	—	48	良好	382	—
355	77	—	—	68.5	2.0	29.5	44	良好	377	688

#### 【0078】実施例1

参考例1で不融化温度を355℃として得た不融化物に、同じく参考例1で溶剤抽出によって得た高軟化点ピッチの繊維状粉末を、不融化物と高軟化点ピッチの混合総重量に対する高軟化点ピッチの量が、0、20、30、40、60、80、および100%となるように混合し、合計量を10gとした。十分混合した後、これにキシレン6mlを加え高軟化点ピッチを溶解、混練し、次いで、60℃で減圧乾燥して混合物からキシレンを除去した後、乳鉢で軽く粉碎して全量が35メッシュ以下の成型原料を得た。

【0079】この成型原料を径3mmの金型を備えたペレタイザー(岡田精工(株)N-30型)で成型し、径3mm、長さ約3mmの円柱状ペレットの成型体を得た。

【0080】次いで、この成型体を空气中、昇温速度0.5℃/minで355℃まで昇温し、この温度で1時間保持することにより不融化した。この不融化条件は、

表2

配合比 (wt%)		成型体に対する 炭化物収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
過不融化物	高軟化点ピッチ			
100	0	(成型不能)	—	—
80	20	39	良好	396
70	30	39	良好	385
60	40	40	良好	390
40	60	37	良好	389
20	80	46	不融化時に膨れ	12
0	100	47	不融化時に膨れ	—

#### 【0084】比較例1

実施例1で得た高軟化点ピッチの配合比が20～60%の成型体を、不融化せずそのまま実施例1と同じ条件で炭化して、炭化物を得た。得られた炭化物の外観、収率ならびに参考例1と同様にして測定したBET法比表面積(SA(BET))を表3に示す。

参考例1から明らかなように、高軟化点ピッチが十分炭素を取り込んで過不融化状態となる条件である。

【0081】次に、この成型体の過不融化物を窒素気流中、昇温速度10℃/minで昇温し、1,000℃で1時間保持することにより炭化した。得られた炭化物の外観、収率ならびに参考例1と同様にして測定したBET法比表面積(SA(BET))を表2に示す。

【0082】同表より、不融化物単独では成型不能であること、高軟化点ピッチの配合比が80%以上では不融化時に内部が溶解して膨れ、成型体の形状を維持できなかったこと、また、内部の溶解が発生した物では比表面積の値が著しく小さくなることがわかる。さらには、高軟化点ピッチの配合比が20～60%の範囲で得た炭化物の場合には、参考例1と同様に大きな比表面積が得られることがわかる。

【0083】

【表2】

【0085】同表より、成型後に不融化しなかった場合の炭化物の比表面積は著しく小さい値となることがわかる。

【0086】

【表3】

表 3

配合比 (wt%)		成型体に対する 炭化物収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
過不融化物	高軟化点ピッチ			
80	20	46	良好 やや膨れ、融着 溶解、形状崩れ	0.2
60	40	43		0.2
40	60	39		1.1

## 【0087】参考例2

参考例1で得た径20 $\mu$ の低軟化点ピッチ繊維から、抽出溶剤としてn-ペンタノールを用いる以外は参考例1と同じ方法で抽出、メタノール洗浄、乾燥して高軟化点ピッチの繊維状粉末を得た。このものの収率は低軟化点ピッチ繊維に対して51%であり、その性状は温度勾配法軟化点232℃、キシレン不溶分0%、キノリン不溶分0%、300℃までの加熱減量1.8%、元素分析値はC92.8%、H7.1%、S0.02%、H/C原子比0.91であった。

【0088】について、この高軟化点ピッチの繊維状粉末を空气中、昇温速度0.5℃/minで加熱し、255℃、305℃、355℃、395℃の所定温度で1時間保持することにより不融化处理し、さらにこの不融化物を窒素気流中、昇温速度10℃/minで加熱し、1,000℃で1時間保持することにより炭化した。不融化物の収率と性状ならびに炭化物の収率と性状を表4に示す。

す。得られた炭化物の比表面積については参考例1と同様にBET法比表面積(SA(BET))およびLangmuir法比表面積(SA(Lang))を測定した。

【0089】不融化温度を255℃としたものを1,000℃で炭化すると、比表面積は小さく気孔の生成は殆ど認められないが、不融化温度を305℃、355℃、395℃と高くしたものでは大きな比表面積が観測され、微細な気孔が生成していることがわかる。

【0090】なお、不融化温度305℃および355℃の吸着等温線は図1と同様、相対圧(P/Ps)の低いところで殆どの吸着が起こっているものであり、また、そのデータからHK法によって細孔分布を計算すると、いずれも細孔径の中心が約6Åにあるシャープな分布をした気孔であることが確認された。

## 【0091】

【表4】

表 4

不融化温度 ℃	不融化物の収率と性状						炭化物の収率と性状			
	収率 wt%	不溶分 wt%		元素分析値 wt%			収率 wt%	外観	比表面積 m <sup>2</sup> /g	
		キシレン	キノリン	C	H	O			SA(BET)	SA(Lang)
255	103	100	100	—	—	—	61	良好	0.2	0.5
305	93	—	—	68.2	2.2	29.6	51	良好	37.1	53.9
355	77	—	—	67.7	2.0	30.3	40	良好	38.5	63.8
395	36	—	—	—	—	—	17	良好	39.8	—

## 【0092】実施例2

参考例2で不融化温度を355℃として得た不融化物7gに同じく参考例2で得た高軟化点ピッチ3gを混合し、これにキシレン3mlを加えて高軟化点ピッチを溶解、混練した。これを実施例1と同様に60℃で減圧乾燥後、乳鉢で粉碎して35メッシュ以下の粉末状の成型原料を得た。さらに、このものを実施例1と同じペレタイザーで成型して径3mm、長さ約3mmの円柱状ペレットの成型体を得た。

【0093】次いで、この成型体を空气中、昇温速度0.5℃/minで昇温し、255℃、305℃および355℃の所定温度で1時間保持することにより不融化し、この不融化された成型体を実施例1と同様に炭化温度1,000℃で炭化して、炭化物を得た。得られた炭

化物の外観、収率ならびに参考例1と同様に測定したBET法比表面積(SA(BET))を表5に示す。

【0094】同表より、成型体の不融化温度を255℃としたものを1,000℃で炭化すると、成型体全体としての比表面積が小さくなること、過不融化石状態とした場合には、その比表面積は参考例2に示した繊維状炭素粉末の比表面積とほぼ同等になることがわかる。なお、不融化温度355℃で得た炭化物については、参考例1と同様にLangmuir法による比表面積(SA(Lang))を測定したところ650m<sup>2</sup>/gであった。

【0095】また、同炭化物の液体窒素温度における窒素の吸着脱着等温線を図2に示す。同図から、得られた成型体は、相対圧(P/Ps)が非常に小さい領域で殆どの吸着が起こっていること、すなわち分布のシャープ

な非常に微細な気孔が生成していることがわかる。なお、図2は参考例1の図1と殆ど同様の吸着脱着等温線を示しており、このことから粉末状態でも本発明の方法に従って得た成型体の場合でも殆ど同様の気孔が生成していることがわかる。このデータから参考例1と同様に

してHK法によって細孔分布を計算したところ約6Åに細孔径の中心があるシャープな分布をした気孔であることが確認された。

【0096】

【表5】

表 5

成型体の不融化温度 (°C)	成型体に対する 炭化物収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
255	4.9	良好	264
305	4.6	良好	368
355	3.8	良好	386

### 【0097】実施例3

参考例2で不融化温度を255°Cとして得た不融化物7gに同じく参考例2で得た高軟化点ピッチ3gを混合し、これにキシレン3mlを加え高軟化点ピッチを溶解、混練した。これを実施例1と同様に60°Cで減圧乾燥後、乳鉢で粉碎して35メッシュ以下の粉末状の成型原料を得た。さらに、実施例1と同じペレタイザーで成型して径3mm、長さ約3mmの円柱状ペレットの成型体を得た。次いで、この成型体を空气中、昇温速度0.5°C/minで昇温し、355°Cで1時間保持することにより不融化し、この不融化された成型体を実施例1と同様に1,000°Cで炭化して、炭化物を得た。得られた炭化物の外観は良好であり、成型体に対する炭化物収率は39%、BET法比表面積(SA(BET))は393m<sup>2</sup>/g、Langmuir法比表面積(SA(Lang))は688m<sup>2</sup>/gであった。

【0098】また、同炭化物の液体窒素温度における窒素の吸着脱着等温線を図3に示す。同図から、得られた成型体は、相対圧(P/Ps)が非常に小さい領域で殆ど吸着が起こっていること、すなわち分布のシャープな非常に微細な気孔が生成していることがわかる。なお、図3は参考例1の図1ならびに実施例2の図2と殆ど同様の吸着脱着等温線を示しており、このことから同炭化物には分布のシャープな微細孔が生成していることがわかる。

【0099】また、このデータから参考例1と同様にし

てHK法によって細孔分布を計算したところ約6Åに細孔径の中心があるシャープな分布をした気孔であることが確認された。

### 【0100】実施例4

参考例1で不融化温度を355°Cとして得た過不融化物に同じく参考例1で溶剤抽出によって得た高軟化点ピッチの繊維状粉末を所定の比率で加え、合計量を10gとした。十分混合した後、これにキシレン6mlを加え高軟化点ピッチを溶解し、混練した。次いで、60°Cで減圧乾燥して混合物からキシレンを除去した後、乳鉢で軽く粉碎して全量が60メッシュ以下の成型原料を得た。この成型原料を内径6mmの金型を用い、総荷重133kgで成型し、径6mm、長さ約6mmの円柱状ペレットの成型体を得た。次いで、この成型体を空气中、昇温速度0.5°C/minで355°Cまで昇温し、この温度で1時間保持することにより不融化した。この不融化条件は参考例1から明らかなように、高軟化点ピッチが十分酸素を取り込んで過不融化状態となる条件である。

【0101】次に、この成型体の過不融化物を窒素気流中、昇温速度10°C/minで昇温し、1,000°Cで1時間保持することにより炭化した。得られた炭化物の外観、収率ならびにBET法比表面積(SA(BET))を表6に示す。加圧成型による成型体でも実施例1と同様に大きな比表面積が得られることがわかる。

【0102】

【表6】

表 6

配合比 (wt%)		成型体に対する 炭化物収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
過不融化物	高軟化点ピッチ			
80	20	3.9	良好、やや脆い	411
70	30	3.8	良好	381
60	40	3.7	良好	368
40	60	3.5	良好	384

### 【0103】参考例3

参考例2でn-ペンタノールで抽出して得た高軟化点ピッチ繊維を空气中、昇温速度0.5°C/minで355°Cまで加熱し、355°Cで1時間保持することにより不融

化し、さらにこの不融化物を窒素気流中、昇温速度10°C/minで加熱し、400~1,500°Cで1時間保持することにより炭化した。得られた炭化物の元素分析、BET法比表面積(SA(BET))およびLangmuir法比

表面積 (SA (Lang)) を表7に示す。

【0104】同表の結果から、窒素吸着で測定される気孔は炭化温度が400℃を越えた時点から急激に生成し、1,100℃を越えた時点で急激に消滅することがわかる。また、BELSORP-28SA型により測定した吸着等温線の結果から、炭化温度600~1,100℃

表7

炭化温度 ℃	元素分析値 (wt%)			比表面積 (m <sup>2</sup> /g)	
	C	H	O	SA (BET)	SA (Lang)
400	70.2	2.1	27.8	2.2	—
500	79.5	2.0	18.4	373	—
600	90.5	2.0	7.5	380	753
800	96.5	0.6	2.8	390	774
1000	99.4	0.2	0.1	385	638
1100	99.8	0.1	0.0	329	553
1200	—	—	—	5.5	—
1300	—	—	—	0.8	—
1500	—	—	—	0.3	—

#### 【0106】実施例5

参考例2で不融化温度を355℃として得た不融化物7gに同じく参考例2で得た高軟化点ピッチ3gを混合し、これにキシレン3mlを加えて高軟化点ピッチを溶解、混練した。これを実施例1と同様に60℃で減圧乾燥後、乳鉢で粉碎して35メッシュ以下の粉末状の成型原料を得た。このものを実施例1と同じペレタイザーで成型して径3mm、長さ約3mmの円柱状ペレットの成型体を得た。次いで、この成型体を空气中、昇温速度0.5℃/minで昇温し、355℃で1時間保持することにより不融化した。さらに、この不融化された成型体を窒素気流中、昇温速度10℃/minで、400~1,300℃

表8

成型体の不融化温度 (℃)	成型体に対する 炭化物収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
400	67	良好	8.3
600	44	良好	403
800	39	良好	402
1000	38	良好	386
1150	37	良好	178
1300	37	良好	2.4

#### 【0109】参考例4

参考例1と同じナフサ分解副生油を蒸留して温度勾配法軟化点49℃の低軟化点ピッチを得た。この低軟化点ピッチ70重量部にキシレン30重量部を添加して溶解し、低軟化点ピッチの溶液を調製した。次に、非イオン系界面活性剤 (ポリオキシエチレンノニルフェニルエーテル、花王製エマルゲン985) 2%を含む水を分散媒とし、膜乳化試験装置 (伊勢化学製) を用い、細孔径4μmのマイクロポラスグラスを分散メディアとして、上記低軟化点ピッチの溶液をこの分散メディアを通して分散媒中に押し出すことにより、低軟化点ピッチ溶液が水中に11容量%分散したいわゆるO/W型エマルジョンを

0℃のものはいずれも中心径が約6Åのシャープな分布の微細孔をもつ多孔質炭素材料であることが確認された。

#### 【0105】

【表7】

℃の所定の温度で1時間保持し、炭化物を得た。得られた炭化物の外観、収率ならびにBET法比表面積 (SA (BET)) を表8に示す。

【0107】同表より、炭化温度が低い場合 (400℃) や高すぎる場合 (1,150℃、1,300℃) には比表面積が小さくなること、および、炭化温度が600、800、1,000℃で得られた炭化物の比表面積は、参考例3で示した炭化物とほぼ同等に大きなものとなることからわかる。

#### 【0108】

【表8】

調製した。

【0110】次に、このエマルジョンを10倍量のSBA中に攪拌しながら徐々に滴下して、低軟化点ピッチ中の可溶成分と溶解のために用いたキシレンを抽出した。この混合液を遠心分離して固形分を得、メタノールで洗浄後、乾燥した。さらに、この固形分を20倍量のn-ペンタノール中に入れて攪拌し、濾過後にメタノールで洗浄して、乾燥し、高軟化点ピッチの球状粒子を得た。このものの低軟化点ピッチに対する収率は48%であった。得られた高軟化点ピッチは平均粒子径が16μmであり、その性状は温度勾配法軟化点243℃、キシレン不溶分0%、キノリン不溶分0%、300℃までの加熱減

量1.7%、元素分析値はC92.7%、H7.1%、S0.02%、H/C原子比0.92であった。

【0111】このものを、参考例1と同様に355℃で1時間不融化し、さらに1,000℃で1時間炭化して球状炭素粒子を得た。不融化、炭化時の収率はn-ペンタノール抽出後の高軟化点ピッチ粒子を基準にしてそれぞれ72%、40%であり、得られた炭素粒子のBET法比表面積(SA(BET))は375m<sup>2</sup>/gであった。

#### 【0112】実施例6

参考例4でエマルジョン化により得た球状粒子の不融化物6gに、同じく参考例4で得た高軟化点ピッチの球状粒子4gを混合し、これにベンゼン4mlを加えて高軟化点ピッチを溶解、混練した。その後、実施例1と同様にして60℃で減圧乾燥後、粉碎して35メッシュ以下の成型原料を得た。このものを実施例1と同じペレタイザーで成型して径3mm、長さ約3mmの円柱状ペレットの成型体を得た。

【0113】次いで、この成型体を空气中、昇温速度0.5℃/minで昇温し、355℃で1時間保持することにより不融化し、さらに、実施例1と同様に1,000℃で炭化して、炭化物を得た。得られた炭化物の外観は良好であり、成型体に対する炭化物収率は38%、BET法比表面積(SA(BET))は383m<sup>2</sup>/gであった。

#### 【0114】実施例7

参考例2で不融化温度を355℃として、1,000℃で炭化して得た炭化物7gに同じく参考例2で得た高軟化点ピッチ3gを混合し、これにキシレン3mlを加えて高軟化点ピッチを溶解、混練した。これを実施例1と同様に60℃で減圧乾燥後、乳鉢で粉碎して35メッシュ以下の粉末状の成型原料を得た。このものを実施例1と同じペレタイザーで成型して径3mm、長さ約3mmの円柱状ペレットの成型体を得た。次いで、この成型体を空气中、昇温速度0.5℃/minで昇温し、355℃で1時間保持することにより不融化し、さらに、実施例1と同様に1,000℃で炭化して、炭化物を得た。

【0115】得られた炭化物の外観は良好であり、成型体に対する収率は72%、BET法比表面積(SA(BET))は409m<sup>2</sup>/g、Langmuir法比表面積(SA(Lang))は848m<sup>2</sup>/gであった。また、このデータから参考例1と同様にしてHK法によって細孔分布を計算したところ約6Åに細孔径の中心があるシャープな分布をした気孔であることが確認された。

#### 【0116】比較例2

実施例7で得た円柱状ペレットの成型体を不融化することなく、そのまま実施例1と同じ条件で1,000℃で炭化して、炭化物を得た。炭化物の成型体に対する収率は72%であり、その形状は良好であったが、BET法比表面積(SA(BET))は42m<sup>2</sup>/gと小さなものであった。

#### 【0117】参考例5

参考例2で不融化温度255℃で処理して得た不融化物を参考例3と同様にして窒素気流中、昇温速度10℃/minで加熱し、500～1,000℃の所定温度で1時間保持することにより炭化した。この不融化物の炭化処理では、炭化炉から出てくる排ガスが300℃付近から白く濁ってくると同時に、炉心管出口部分の内部に茶色から黒褐色のタール状物が付着してくることが観測された。また、得られた炭化物の繊維状高軟化点ピッチに対する収率およびBET法比表面積(SA(BET))を表9に示す。同表の結果から、酸素濃度の飽和していない不融化物を炭化した場合、600～800℃という狭い炭化温度範囲では比較的大きな比表面積が観測されるが、それ以下、もしくはそれ以上の温度では比表面積が急激に小さくなっていることがわかる。

#### 【0118】

【表9】

炭化温度 ℃	高軟化点ピッチに対する炭化物収率 (wt%)	比表面積 SA(BET) (m <sup>2</sup> /g)
500	71	59
600	66	32.8
800	63	29.8
900	62	18.5
1000	61	0.2

#### 【0119】実施例8

参考例2で不融化温度255℃で処理して得た不融化物14gに、同じく参考例2で得た高軟化点ピッチの繊維状粉末6gを混合し、これにキシレン6mlを加えて高軟化点ピッチを溶解、混練した。これを実施例1と同様に60℃で減圧乾燥後、乳鉢で粉碎して20メッシュ以下の粉末状の成型原料を得た。さらに、このものを実施例1と同じペレタイザーで成型して径3mm、長さ約3mmの円柱状ペレットの成型体を得た。次いで、この成型体を空气中、昇温速度0.5℃/minで昇温し、255℃で1時間保持することにより不融化し、さらにこの不融化物を窒素気流中、昇温速度10℃/minで昇温し、600℃、800℃および1,000℃の各温度で1時間保持することにより炭化した。

【0120】得られた炭化物の成型体に対する収率およびBET法比表面積を表10に示す。同表から、フィラーの不融化、成型体の不融化をいずれも255℃で行い酸素濃度の飽和していない不融化物を炭化した場合、炭化温度600～800℃では大きな比表面積が観測されるが、炭化温度1,000℃では比表面積が減少することがわかる。従って、より広い炭化温度範囲で大きな比表面積を持つ炭化物を得るには、成型体を過不融化状態とする方が好ましいことがわかる。

#### 【0121】



【表10】

表 10

炭化温度 ℃	成型体に対する 炭化物収率 (wt%)	比表面積 SA(BET) ( $\text{m}^2/\text{g}$ )
600	6.2	336
800	5.9	336
1000	5.9	77

## 【0122】

【発明の効果】本発明の方法によれば、安価な重質油またはそれから得られる低軟化点ピッチ等を出発原料とし、また、まず出発原料の重質油等を賦形した後、溶剤抽出により高軟化点化を図るという方法を採用するため、従来高軟化点ピッチを製造する際に問題となっていた例えば原料の高価さや、高温の加熱処理に伴う経済的、技術的問題を回避することができ、さらに、同一の

出発原料から得られるフィラーおよびバインダーを使用するため、従来の方法では得られなかった均質な炭素で構成され、かつ、均一な微細孔を持つ多孔質炭素成型体を工業的に簡便で効率よく得ることができる。また、本発明方法により得られる成型体は均質でかつ均一な微細孔を持つため分子吸着剤、触媒、電極炭素等として有用である。

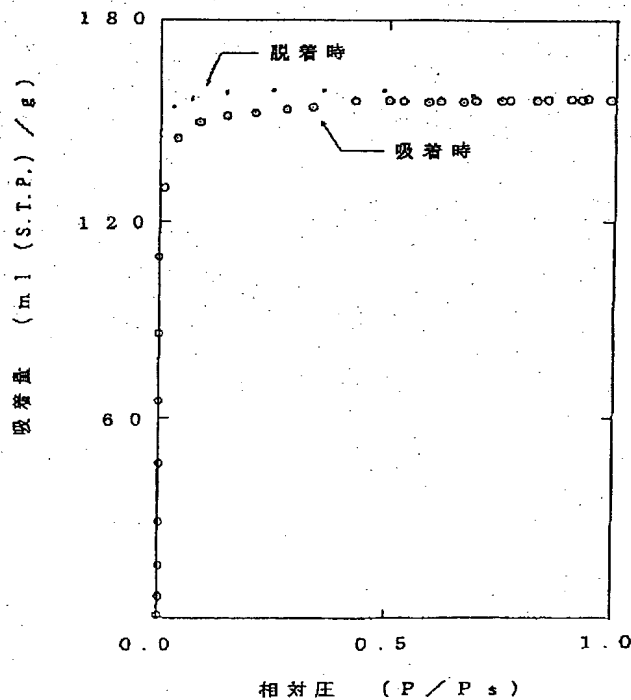
## 【図面の簡単な説明】

【図1】参考例1において、不融化温度を355℃とした場合の多孔質炭素材料の液体窒素温度における窒素の吸着脱着等温線である。

【図2】実施例2において、第6工程の不融化温度を355℃として得た多孔質炭素成型体の液体窒素温度における窒素の吸着脱着等温線である。

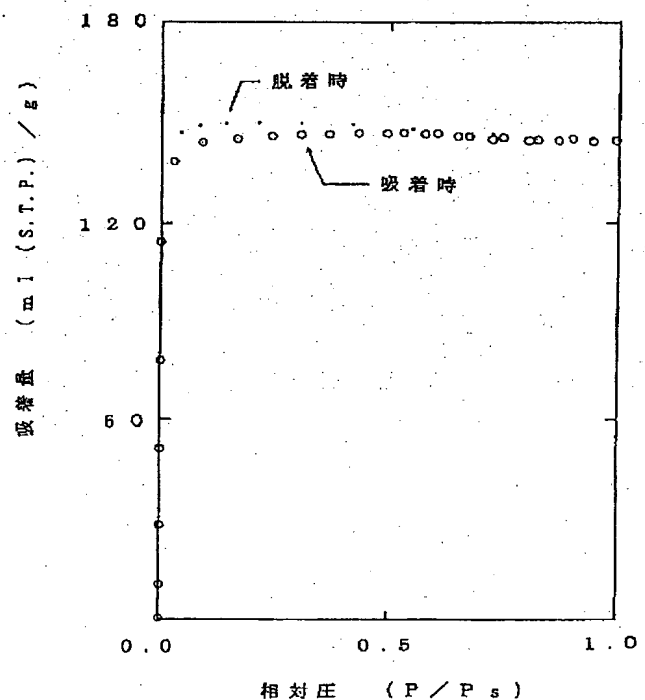
【図3】実施例3で得た多孔質炭素成型体の液体窒素温度における窒素の吸着脱着等温線である。

【図1】



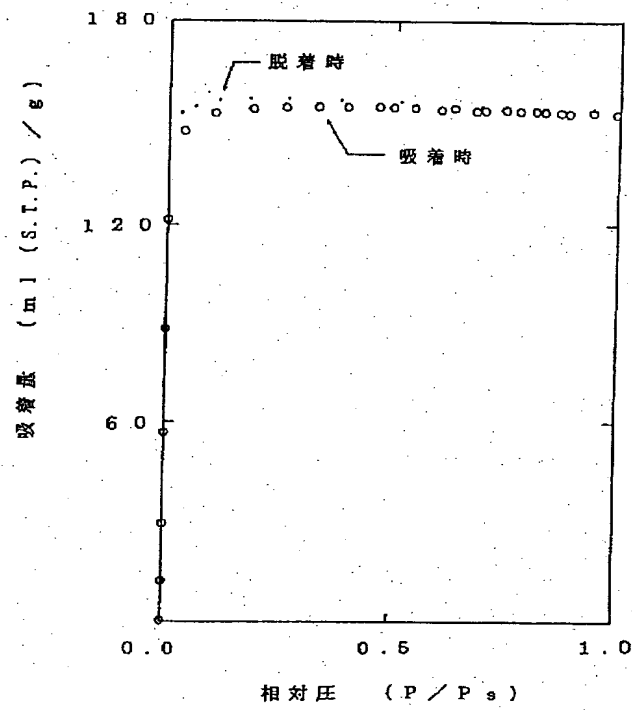
窒素の吸着脱着等温線 (77 K)

【図2】



窒素の吸着脱着等温線 (77 K)

【図3】



窒素の吸着脱着等温線 (77 K)

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-188565

(43)Date of publication of application : 22.07.1997

(51)Int.Cl.

C04B 35/52

C01B 31/02

C10C 3/04

C10C 3/10

(21)Application number : 08-018327

(71)Applicant : MARUZEN PETROCHEM CO LTD

(22)Date of filing : 09.01.1996

(72)Inventor : TSUCHITANI MASATOSHI

NAKAJIMA RYOICHI

SUZUKI SEIKI

SHIGEMATSU HITOSHI

NISHITANI KATSUTOSHI

(54) POROUS CARBON FORMED BODY HAVING UNIFORM FINE PORE AND PRODUCTION OF THE SAME

(57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a porous carbon formed body having uniform fine pores by forming a mixture of a specific filler of an infusible substance with a pitch having a high softening point, performing a treatment for making it infusible, burning and carbonizing.

**SOLUTION:** This porous carbon formed body having uniform fine pores having  $\geq 3002$  BET specific surface area and  $\leq 10\text{\AA}$  middle pore diameter, is obtained by first obtaining a pitch having a high softening point (A) having  $\geq 180^\circ\text{C}$  softening point and  $\leq 5\text{wt.}\%$  heat loss at  $\leq 300^\circ\text{C}$  by bringing a formed body obtained by forming a heavy oil having 0.8–1.2 C/H atomic ratio and not containing a portion insoluble to a BTX solvent or a pitch having a low softening point of  $\leq 150^\circ\text{C}$  softening point measured by a temperature gradient method into a particle-like, a powder-like or a fiber-like shape having  $\leq 100\mu\text{m}$  diameter into contact with an organic solvent capable of leaving  $\geq 10\text{wt.}\%$  as an insoluble portion for extracting a light component, then, obtaining an infusible component (B) by performing a treatment to make the component (A) infusible under an atmosphere not containing oxygen, and next, by mixing the component (A) with 20–70wt.% component (B), forming so as to become  $\leq 5\text{mm}$  minimum distance from its center to the outer surface thereof, performing the treatment for making the same infusible under the atmosphere not containing oxygen, burning under an inert atmosphere and carbonizing.

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

[Claim(s)]

[Claim 1] Temperature gradient method softening temperature obtained from heavy oil which has a H/C atomic ratio in the range of 0.8-1.2 Not less than 180 \*\*, A non-deliqescence thing which loss on heating up to 300 \*\* is 5 or less % of the weight, and carried out non-deliqescence [ of the high softening point pitch which does not contain BTX solvent insoluble matter substantially ] is made into a filler. Temperature gradient method softening temperature obtained from heavy oil which has a H/C atomic ratio in the range of 0.8-1.2 Not less than 180 \*\*. Loss on heating up to 300 \*\* is 5 or less % of the weight, and a high softening point pitch which does not contain BTX solvent insoluble matter substantially is used as a binder. A porous carbon molding body in which specific surface area by a BET adsorption method using nitrogen absorption which molds, considers it as a molding body and is obtained non-deliqescence and by carbonizing in this is more than 300-m<sup>2</sup>/g, and a main pole diameter has the uniform micropore which comprised homogeneous carbon of 10A or less.

[Claim 2] Temperature gradient method softening temperature produced from heavy oil characterized by comprising the following which a H/C (starting material) atomic ratio is in the range of 0.8-1.2, and does not contain BTX solvent insoluble matter substantially, or this heavy oil by distilling off a more volatile component is 150 \*\* or less.  
The 1st process that uses as a starting material a low softening point pitch which does not contain BTX solvent insoluble matter substantially, carries out size enlargement of this (the 1st process) starting material to particle state with a diameter of 100micro or less, and powdered or fibrous, and is used as a size enlargement object.

(The 2nd process) By contacting this size enlargement object to an organic solvent which may be made to remain as insoluble matter that at least 10% of the weight, a more volatile component is extracted and temperature gradient method softening temperature is not less than 180 \*\*. And the 2nd process that loss on heating up to 300 \*\* is 5 or less % of the weight, and is made into a high softening point pitch which does not contain BTX solvent insoluble matter substantially, and by which size enlargement was carried out.  
(The 3rd process) The 3rd process of carrying out non-deliqescence processing of this high softening point pitch by which size enlargement was carried out in atmosphere containing oxygen, and obtaining a non-deliqescence thing filler.

(The 4th process) A high softening point pitch obtained at the 2nd process by this non-deliqescence thing filler, and a high softening point pitch manufactured similarly. After mixing so that quantity of a high softening point pitch to mixed gross weight of a non-deliqescence thing filler and a high softening point pitch may be 20 to 70 % of the weight, it grinds if needed, it is [ the 4th process of obtaining a molding material which uses a high softening point pitch as a binder, the 5th process, at which this (the 5th process) molding material is molded into, and the shortest distance to an outside surface obtains a molding body of 5 mm or less from the central part, and ] oxygen about this (the 6th process) molding body.

[Claim 3] A manufacturing method of a porous carbon molding body with the uniform micropore according to claim 2 which are the conditions that non-deliqescence conditions of the 6th process

are severer than conditions with which an oxygen density in this non-deliqescence thing is saturated, and is a temperature requirement whose carbonization temperature of the 7th process is 500-1,100 \*\*.

[Claim 4] Heavy oil which carries out a byproduction when heavy oil of a starting material carries out the pyrolysis of naphtha or the gas oil and olefins are manufactured. Or a manufacturing method of a porous carbon molding body with the uniform micropore according to claim 2 or 3 which is at least one kind of petroleum system decomposition heavy oil chosen from heavy oil which carries out a byproduction when carrying out fluidized catalytic cracking of the petroleum and reforming it.

[Claim 5] A manufacturing method of a porous carbon molding body in which how to carry out size enlargement of the 1st process has a certain uniform micropore according to any one of claims 2 to 4 by grinding of a starting material, melt spinning, or emulsion-ization.

[Claim 6] A manufacturing method of a porous carbon molding body in which an organic solvent of the 2nd process has the uniform micropore according to any one of claims 2 to 5 which are paraffin hydrocarbon, alcohols, ketone, or a partially aromatic solvent that mixes these.

[Claim 7] This organic solvent N-pentane, cyclopentane, n-hexane, an isohexane, Cyclohexane, n-heptane, isooctane, methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, A manufacturing method of a porous carbon molding body with the uniform micropore according to claim 6 which is at least one sort chosen from n-pentanol, n-hexanol, cyclohexanol, acetone, methyl ethyl ketone, a diethyl ketone, methyl isopropyl ketone, and methyl isobutyl ketone.

[Claim 8] A manufacturing method of a porous carbon molding body which has how to carry out size enlargement of the 1st process by emulsion-ization and in which an organic solvent of the 2nd process has the uniform micropore according to any one of claims 2 to 4 which are alcohols, ketone, or a partially aromatic solvent that mixes these.

[Claim 9] This organic solvent Methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, n-pentanol, n-hexanol, A manufacturing method of a porous carbon molding body with the uniform micropore according to claim 8 which is at least one sort chosen from cyclohexanol, acetone, methyl ethyl ketone, a diethyl ketone, methyl isopropyl ketone, and methyl isobutyl ketone.

[Claim 10] A manufacturing method of a porous carbon molding body in which a porous carbon molding body with uniform micropore has the uniform micropore according to any one of claims 2 to 9 whose specific surface area by a BET adsorption method using nitrogen absorption is more than 300-m<sup>2</sup>/g and, whose main pole diameter is 10A or less.

[Translation done.]

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a porous carbon molding body with the uniform micropore used for a molecular adsorption agent, a catalyst, electrode carbon, etc., and a manufacturing method for the same.

[0002]

[Description of the Prior Art] The method of using a carbon material with a stoma very as detailed as 10A or less for nitrogen in the air or the separate recovery of carbon dioxide attracts attention in recent years, PSA which performs adsorption desorption of gas according to a pressure differential Law (Pressure Swing Adsorption). And development of the porous carbon material called MSC (Molecular Sieving Carbon) used for this use or CMS (Carbon Molecular Sieve) is prosperous.

[0003] Also about the negative-electrode carbon for lithium ion batteries in which art and a commercial scene spread out quickly recently. There is a report (for example, carbonaceous pore structure, the collection of "battery capacity" 1994 Carbon Society of Japan gists, p190-191) that carbonaceous pore structure is related to cell capacity, and the porous carbon in which the electrode carbon used for an electrical double layer capacitor also has micropore further is used.

[0004] Thus, the deployment to a use new besides conventional adsorbent and catalyst is spreading, and the case of a porous carbon material further used as molding bodies, such as a grain, tabular, or a pellet type, is also increasing. For this reason, in the case of detailed particles, powder, or a fibrous carbon material, in addition to development of the method of controlling the pore structure of the carbon material itself, and pore distribution, development of the manufacturing method of a porosity molding body is also performed.

[0005] For example, it grinds, after carrying out demineralization acid treatment of the vinylidene chloride system copolymer waste. To this, a sintering agent and APISERU, such as a coal tar pitch, asphalt, and caking coal. How to blend and corn granulation agents, such as blackstrap molasses and sulfite pulp, and carbonize in an inert atmosphere (JP.50-161485.A). The pitch and cellulose crystallite set thing whose softening temperature it grinds and is 50-150 ° in this after carrying out demineralization acid treatment of the vinylidene chloride system polymers, the method (JP.52-75691.A) of blending and corning a water soluble cellulose derivative or sugars, and carbonizing in an inert atmosphere Make coal tar or a coal tar pitch with a binder JP.52-77017.A and coconut-shell-charcoal powder, and Combination. How to impregnate this with creosote oil and carbonize in an inert atmosphere further after corning and dry-distilling (JP.62-176908.A). Coal tar, a pitch, creosote oil, etc. are blended with powder, such as phenol resin and melamine resin, as a binder. Carry out spinning of the method (JP.4-280810.A) and high softening point pitch which are carbonized in an inert atmosphere after corning, suppose that it is fibrous, after carrying out non-deliquescence, agglomerate granular or spherically, and Polyvinyl alcohol from this mass material, starch, phenol resin. The three-dimensional terminal web-like object on which mass material was pasted up is acquired using a solution or dispersion liquid, such as a pitch, as a binder. How to carbonize this in an inert atmosphere (JP.6-157018.A). After carrying out

spinning of the high softening point pitch, supposing that it is fibrous and carrying out non-deliquescence, softening temperature molds in tabular, using as a binder a pitch, phenol resin, furan resin, etc. which are 80-150 °, and the method (JP.7-81915.A) of carbonizing in an inert atmosphere, etc. are indicated. However, in the above-mentioned method, by the organic matter used as a binder or a binder necessarily not forming micropore by carbonization, when there is a little stoma generation of these carbide, there is a problem of causing decline in the porosity as the whole molding body. This is clear also from "The decline in voidage and degradation of molecular sieve performance are caused, and it is not desirable" being indicated, if the amount of the binder used increases also in JP.6-157018.A and JP.7-81915.A.

[0006] Then, as a method of also giving a stoma intentionally to a binder portion. For example, the pitch whose softening temperature is 80-150 ° after carrying out spinning of the high softening point pitch, supposing that it is fibrous and carrying out non-deliquescence, Phenol resin, furan resin, etc. are molded into a spherical non-deliquescent fiber lump as a binder. How to carbonize in an inert atmosphere after carrying out non-deliquescence processing of this again (JP.6-142503.A). The pitch whose softening temperature is 80-150 ° after grinding a high softening

point pitch, supposing that it is powdered and carrying out non-deliquescence, Phenol resin, furan resin, an epoxy resin, etc. are corned as a binder, and after carrying out non-deliquescence processing of this again, the method (JP.6-144818.A) of carbonizing in an inert atmosphere, etc. are indicated. However, also in the way the carbide which carbonized such a binder or a binder forms micropore, the carbon generated from carbon, binder, or binder which is a filler completely cannot but be heterogeneous, therefore pore structure cannot but serve as an uneven porous carbon molding body.

[0007] As mentioned above, it could not say that development of the efficient and economical manufacturing method of a porous carbon molding body with uniform micropore was still enough, and was hardly conventionally known about a porous carbon molding body which comprised still more homogeneous carbon, and a manufacturing method for the same.

[0008]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to provide the porous carbon molding body which comprises homogeneous carbon and has uniform micropore, and the method of manufacturing this efficiently industrially simple and economically.

[0009]

[Means for Solving the Problem] This invention persons use as a starting material the heavy oil which has specific description previously, and first this Particle state. If it oxidizes under atmosphere containing oxygen, a high softening point pitch which is powdered, or carries out size enlargement to fibrous and is subsequently obtained from this size enlargement object by a method of carrying out extraction removal of the more volatile component by an organic solvent is used as a non-deliquescence thing and carbonization treatment is further carried out under an inert atmosphere. It found out that carbide obtained formed uniform micropore (November 24, Heisei 7 application). In order to attain the above-mentioned purpose this time, as a result of repeating examination wholeheartedly, the further above-mentioned high softening point pitch has moldability and a self-degree of sintering in itself. By making a non-deliquescence thing of this high softening point pitch into a filler, and mixing both by using a high softening point pitch as a binder, it finds out like the above non-deliquescence and that a binder portion and a filler portion will form the same uniform micropore if carbonization treatment is carried out for that a molding body in which a high softening point pitch adhered to the circumference of a filler is obtained easily, and this molding body, and came to complete this invention.

[0010] Temperature gradient method softening temperature obtained from heavy oil which has a H/C atomic ratio in the range of 0.8-1.2 a gist of the first invention Namely, not less than 180 °. A non-deliquescence thing which loss on heating up to 300 ° is 5 or less % of the weight, and carried out non-deliquescence [ of the high softening point pitch which does not contain BTX solvent insoluble matter substantially ] is made into a filler. Temperature gradient method softening temperature obtained from heavy oil which has a H/C atomic ratio in the range of 0.8-1.2 Not less than 180 °. Loss on heating up to 300 ° is 5 or less % of the weight, and a high softening point pitch which does not contain BTX solvent insoluble matter substantially is used

as a binder. Mold, consider it as a molding body and obtain this non-deliquesce and by carbonizing. Specific surface area by a BET adsorption method using nitrogen absorption is more than  $300\text{-m}^2/\text{g}$ . And a main pole diameter consists uniform micropore which comprised homogeneous carbon of 10A or less in a porous carbon molding body which it has, and it and a gist of the second invention. Heavy oil which a H/C atomic ratio is in the range of 0.8-1.2, and does not contain BTX solvent insoluble matter substantially. Use as a starting material a low softening point pitch which temperature gradient method softening temperature produced from this heavy oil by distilling off a more volatile component is 150 ° or less, and does not contain BTX solvent insoluble matter substantially, and this starting material or particle state with a diameter of 100μm or less. By making an organic solvent which is powdered or may make the 1st process that carries out size enlargement to fibrous and is used as a size enlargement object, and this size enlargement object remain as insoluble matter that at least 10% of the weight contact, a more volatile component is extracted and temperature gradient method softening temperature is not less than 180 °. And the 2nd process made into a high softening point pitch which loss on heating up to 300 ° is 5 or less % of the weight, and does not contain BTX solvent insoluble matter substantially, and by which size enlargement was carried out. The 3rd process of carrying out non-deliquesce processing of this high softening point pitch by which size enlargement was carried out in atmosphere containing oxygen, and obtaining a non-deliquesce thing filler. A high softening point pitch obtained at the 2nd process by this non-deliquesce thing filler, and a high softening point pitch manufactured similarly. After mixing so that quantity of a high softening point pitch to mixed gross weight of a non-deliquesce thing filler and a high softening point pitch may be 20 to 70 % of the weight, it grinds if needed. The 4th process of obtaining a molding material which uses a high softening point pitch as a binder, and the 5th process, at which this molding material is molded into and the shortest distance to an outside surface obtains a molding body of 5 mm or less from the central part. Carry out non-deliquesce processing of this molding body in atmosphere containing oxygen, and the 8th process of changing both a filler portion and a binder portion into a non-deliquesce state, and this molding body by which non-deliquesce was carried out are calcinated in an inert atmosphere. It consists in a manufacturing method of a porous carbon molding body with uniform micropore consisting of the 7th process to carbonize.

[0011]A BTX solvent as used in the field of this invention shows benzene, toluene, xylene, and an aromatic solvent like ethylbenzene.

[0012]

[Embodiment of the Invention] Hereafter, it explains still in detail about this invention. (Starting material) In the starting material of this invention, it is required for the ranges of a H/C atomic ratio to be 0.8-1.2. In what has an aliphatic side chain high the thing which has a H/C atomic ratio smaller than 0.8, i.e., aromatic property, and very small. At the time of non-deliquesce [ of the 3rd process and the 6th process ], since the uptake rate of oxygen is slow, In trying to perform non-deliquesce [ to the inside of a size enlargement object and a molding body / sufficient ], and the fault non-deliquesce to the grade with which the oxygen density in a non-deliquesce thing which is mentioned further later is saturated mostly. On the surface, since oxidative consumption will already be in a remarkable quick state and the recovery rate of an object falls, it is inefficient-like, and when there is little uptake quantity of oxygen, melting inside a molding body happens at the time of carbonization of the 7th process, and generation of big specific surface area, i.e., many stoma generation, becomes difficult. On the contrary, the thing which has a larger H/C atomic ratio than 1.2, i.e., aromatic property, is low, and in the very high thing of aliphatic series nature. Since a recovery rate becomes remarkably low at the time of extraction of the more volatile component of the 2nd process and also desorption by decomposition increases more than incorporation of oxygen also in non-deliquesce [ of the 3rd process and the 6th process ], the recovery rate of an object becomes low too.

[0013] That is [ a starting material does not contain an insoluble ingredient in a BTX solvent substantially ], it is important that the value of insoluble matter when it measures by a general insoluble matter measuring method which is specified to JIS is 1 or less % of the weight. When an

insoluble ingredient exists in a BTX solvent, this a starting material. The particle state of micron order. Since it not only becomes an obstacle at the time of powdered or carrying out size enlargement to fibrous, but an ingredient insoluble to these BTXs solvent is an ingredient whose number of fused aromatic rings the molecular weight generated by thermal polymerization etc. is large, namely, is large. When this is contained so much, the quantity of the oxygen incorporated at the time of non-deliquesce will fall, and the fall of stoma generation or decline in yield will be caused by extension. It is because the quantity of oxygen which is naturally equivalent to the edge part of a molecule when the number of fused aromatic rings is large, since oxidation reaction cannot oxidize [ this ] easily from the edge part of a molecule in non-deliquesce [ of heavy oil or pitches ] in the inside of a cause will become a small value if it is seen from the whole molecule.

[0014] In order to use as a binder the high softening point pitch pass the 1st and 2nd process in the method of this invention. When a lot of BTX solvent insoluble matter is contained in the starting material, the problem of a binder not being uniformly mixed from this, including BTX solvent insoluble matter naturally, or the high softening point pitch obtained from this not adhering to a non-deliquesce thing uniformly, either will arise.

[0015] As heavy oil which fulfills the conditions of such this invention, The heavy oil which carries out a byproduct when cracking naphtha and manufacturing olefins (naphtha-cracking byproduct oil). When decomposing a gas oil (gas oil fraction) and manufacturing olefins, there is petroleum system decomposition heavy oil, such as heavy oil (pyrolysis tar) which carries out a byproduct, and heavy oil (a decantation oil or an FCC slurry oil) which carries out a byproduct at the time of fluidized catalytic cracking (FCC) of petroleum. Especially, since a raw material is naphtha primarily, a naphtha-cracking byproduct oil has dramatically little hetero elemental content, such as sulfur, nitrogen, and oxygen, and it is preferred for it also from the field of the flue gas treatment at the time of carbonization.

[0016] Since aromatic property usually contains a lot of BTX solvent insoluble matter quite highly (H/C is small) in the case of Carboniferous system heavy oil like coal tar. Although using then is not preferred, if refining operation is performed so that the conditions of this invention may be suited by processing of separation of BTX solvent insoluble matter, removal, or hydrocracking, it is usable as a starting material of this invention. However, since the cost accompanying refining operation starts in this case, if it compares with the above-mentioned petroleum system heavy oil, it will be hard to call it a desirable raw material.

[0017] Such heavy oil can also be used for the starting material of this invention as it is, and the temperature gradient method softening temperature obtained by removing a more volatile component by distillation operation can also use the low softening point pitch of 150 ° or less. Sample pitch powder is placed on the aluminum board which attached the temperature gradient with temperature gradient method softening temperature here, Although this is discarded by a brush and the position which a sample begins to melt and adheres to the aluminum board surface is searched for, and it is the method (measuring instrument: the product made by the Asia \*\*\*\*\* AMK-B2CEFH-3) of making softening temperature skin temperature of the aluminum board of this point and changes also with the kind of pitch, and character. About, this temperature gradient method softening temperature serves as a value lower 25-50 ° than the Mettler method softening temperature which became a value lower 15-20 ° than the R&B method (ring & ball method) softening temperature specified to JIS, and was specified to ASTM.

[0018] When adopting emulsion-ization as the method of the 1st process mentioned later, remaining as it is, or the thing which carried out viscosity control if needed and the thing which made viscosity low by dissolving in an organic solvent in the case of a low softening point pitch, and considering it as solution form can also be used for the above-mentioned heavy oil. It is preferred that the viscosity at emulsion-ized temperature is 1,000 poise or less in the method by this emulsion-izing. In this case, since these starting materials used by this invention are what does not contain an insoluble ingredient in a BTX solvent, In order to consider it as a solution, it cannot be overemphasized that a BTX solvent is suitable for the organic solvent to be used, but it will become usable if it is an organic solvent which can dissolve 90% of the weight or more of this raw material at least.

[0019](The 1st process) The 1st process of this invention is particle state with a diameter of 100micro or less and a process which powdered or carries out size enlargement to fibrous about the above specific raw materials.

[0020]One of the reasons a path shall be 100micro or less is for making it extraction take place promptly and uniformly in the extraction process of the following more volatile component. If a path is larger than [ for example, ] mm order, although extraction of an outside surface takes place promptly, since it requires time for extraction to an inside, it will become uneven [ an extraction state ] for extraction time to be insufficient. One reason is for changing into a non-deliquesce state to homogeneity to an inside also at the non-deliquesce process after extraction. When a path is large, even if an outside surface will be in a non-deliquesce state, the oxygen diffusion to an inside becomes late and becomes uneven. If melting and weld tend to be caused with subsequent heating as non-deliquesce [ internal ] is insufficient, or it is going to carry out non-deliquesce enough to an inside, a surface portion will be in the state of already starting oxidative consumption, and a recovery rate will fall remarkably as a result.

[0021]The method of size enlargement can adopt various methods, such as grinding, spinning, or emulsion-izing. Since the starting material of this invention has temperature gradient method softening temperature as low as 150 \*\* or less and particles may weld with the heat generated at the time of grinding when based on grinding, it is preferred to grind, cooling, or to grind, mixing with a lot of gas.

[0022]The temperature gradient method softening temperature of a starting material is higher than a room temperature enough, for example, when it is not less than 45 \*\*, it can also be based on spinning. If it heats so that the viscosity may serve as hundreds - 1000 poise of numbers since the starting material used by this invention is what does not contain BTX solvent insoluble matter substantially, melt spinning is easily possible for it. The method of spinning is extruded from a nozzle and can adopt methods, such as a continuous glass fiber manufacturing method which tows and forms this into thin \*\*, a centrifugal spinning method which forms into thin \*\* the pitch extruded from the nozzle according to a centrifugal force, the melt blowing method which passes high-speed gas directly under the nozzle, and is formed into thin \*\* by the power, or an eddy current method. The spinning temperature of the low softening point pitch of this invention whose spinning temperature should just be a temperature higher about 50-70 \*\* than the temperature gradient method softening temperature of the raw material to be used therefore whose temperature gradient method softening temperature is 45-150 \*\* has the preferred range of 95-220 \*\*. Since this temperature region is lower than the temperature region where a common organic matter decomposes and deteriorates enough in inactive gas, it \*\*\*\*\*\*, and the phenomenon of decomposition within a spinning machine which poses a problem in the usual high softening point pitch at the spinning process of the pitch based carbon fiber manufactured as a raw material, deterioration, and a caulking is stabilized, and can carry out spinning. When temperature gradient method softening temperature is comparatively low, if the pitch textiles which came out from the nozzle hole are not cooled enough, textiles may weld, but in such a case, weld of textiles can be prevented by coming out from a nozzle hole and dropping the pitch textiles formed into thin \*\* into the organic solvent directly used at the 2nd process. [0023]Softening temperature is lower than 45 \*\*, or at ordinary temperature, when liquefied, the means of such grinding or spinning cannot be adopted as the method of size enlargement, but emulsion-ization performs. About the method of emulsion-izing, this invention persons are indicating in Japanese Patent Application No. 331132 [ six to ] previously. Namely, when this raw material heavy oil is not in the state concerned in a liquefied state with a viscosity of 1,000 poise or less in "raw material heavy oil. Do not dissolve with a means to heat, or water, and the state of this raw material heavy oil is prepared in the state concerned according to concomitant use of a means to dilute thru/or dissolve raw material heavy oil by the organic solvent which dissolves 90% of the weight or more, or this both-hands stage, it can agitate with water under existence of a surface-active agent with the agitation means by which shearing force is given, and size enlargement can be carried out by the method of this raw material heavy oil making it the emulsion underwater distributed as a detailed spherical particle 100micro or less in diameter."

[0024]The feature of this method is once changing heavy oil and pitches into an emulsion state, underwater, and it is the size enlargement method by which the heavy oil in an emulsion state used becoming spherical with that surface tension. The film emulsification method developed recently in addition to the method of the above-mentioned "churning to which shearing force is given" can also be adopted as the above-mentioned emulsion-ization. This method makes glass\* or ceramics with the fine pores of uniform micron order emulsification film media. The water which contains in one side of these emulsification film media the surface-active agent which is carrier fluid is put in, and it circulates or agitates, and is the method of extruding underwater the solution which dissolved the heavy oil, pitches, or pitch which is a dispersoid in the organic solvent, and was diluted according to a pressure differential from the opposite hand of emulsification film media. When extruding, since a dispersoid passes the uniform fine pores of emulsification film media, it distributes underwater as particles proportional to the size of the fine pores, therefore it can obtain an emulsion particle with very sharp particle size distribution. [0025]Particles, powder, or a fibrous size enlargement object with a diameter of 100micro or less can be acquired easily as mentioned above, the state where the microscopic particles by which the path of a size enlargement object is too small, for example, less than 0.1 micro are contained so much considers the handling at the time of non-deliquesce [ next ] and carbonization — rich — carry out — although it is not desirable, the path of the size enlargement object acquired by the above-mentioned method is usually 0.1micro or more.

[0026](The 2nd process) The 2nd process of this invention is a process of obtaining the high softening point pitch by which size enlargement was carried out to the particles, the powder, or fibrous which has description required since non-deliquesce advances without trouble in the following non-deliquesce process. That is, since it is about 140-160 \*\*, if the oxidation starting temperature under the air atmosphere of the pitch manufactured from petroleum system decomposition heavy oil has the softening point of pitch lower than this temperature, melting of a pitch and weld will take place and it will usually become difficult [ non-deliquesce ]. therefore, the softening point of pitch in front of non-deliquesce is higher than this value enough — not less than 200 \*\* of not less than at least 180 \*\* is preferably required. In the thing that the loss on heating up to 300 \*\* of a pitch exceeds 5 % of the weight, there is a possibility that an organic matter may volatilize so much from a pitch, and it is not desirable from a safety aspect at the same time the problem of melting and weld similarly arises in a non-deliquesce process. Therefore, 3 or less % of the weight is preferably required for the loss on heating up to 300 \*\* of the pitch in front of non-deliquesce 5 or less % of the weight.

[0027]The organic solvent used for such the purpose although an organic solvent extracts a more volatile component from that by which size enlargement was carried out at the 1st process in the 2nd process requires that at least 10% of the weight of a starting material should be a thing which may be made to remain as insoluble matter. If a soluble high organic solvent is used more than this, since the shape which the recovery rate of the high softening point pitch obtained fell, and efficiency not only worsens, but carried out size enlargement at the 1st process may collapse, it is not desirable.

[0028]Paraffin hydrocarbon, ketone, or alcohols are mentioned to the organic solvent with which it is satisfied of the above conditions. As paraffin hydrocarbon, as ketone n-pentane, cyclopentane, n-hexane, an isohexane, cyclohexane, n-heptane, isooctane, etc. for example, As alcohols, acetone, methyl ethyl ketone (MEK), a diethyl ketone, methyl isopropyl ketone, methyl isobutyl ketone (MIBK), etc. for example, Methanol, ethanol, n-propanol, isopropanol (IPA), n-butanol, sec-butanol (SBA), n-pentanol, n-hexanol, cyclohexanol, etc. are mentioned, and these are independent. Or it is used as a partially aromatic solvent which was mixed and was adjusted to suitable solubility.

[0029]Since a SCUM-like thing will arise and separation will become difficult if a paraffin hydrocarbon solvent is independently used for example, it does not dissolve with water when it emulsion-izes at the 1st process, use of the alcohols which form the water and the uniform layer in the above-mentioned organic solvent, and ketone is preferred in this case.

[0030]The method in particular of extraction of a more volatile component is not limited, and should just adopt the method usually known. Since size enlargement of the raw material has

already been carried out to 100micro or less in the case of this invention, the raw material by which size enlargement was carried out, for example is agitated with an organic solvent, and it is promptly extracted by the method of filtering and centrifuging this and collecting insoluble matter. Although what is necessary is just to choose the solvent amount used at this time in [ of a raw material ] tens of [ several to ] times the amount, Since the quantity which will be extracted if there is little amount of the solvent used is limited, and softening temperature may not become high enough, or the mobility after mixing may worsen and it may interfere with extract operation when the path of the particles by which size enlargement was carried out is small, it is desirable to usually use an about 3-30-times the amount solvent. Although the temperature at the time of extraction is enough near a room temperature, warming in order to make solubility high is also possible. Although extraction time in particular is not limited, either, it is usually enough in several or less hours. Since removal of a solvent and desiccation of a pitch take time when the high solvent of the boiling point is used, In this case, after removing the used solvent enough by methods such as filtration, it is also a desirable method to dry, after a solvent with solubility lower than that solvent and the low boiling point washes and removing the high solvent of the boiling point. Extract operation is not limited at once, may repeat operation of extraction and separation, and may be performed.

[0031]Not less than 180 \*\* of temperature gradient method softening temperatures are not less than 200 \*\* preferably as mentioned above, and the loss on heating up to 300 \*\* can obtain easily 3 or less % of the weight of a high softening point pitch preferably 5 or less % of the weight.

[0032]The high softening point pitch pass and by which size enlargement was carried out the 1st process and the 2nd process of this invention, Temperature gradient method softening temperature is not less than 180 \*\*, and in respect of softening temperature, in spite of being comparable as the spinning pitch for carbon fiber, Loss on heating also differs from the spinning pitch for carbon fiber in that it is said that it is few excluding the insoluble ingredient in the BTX solvent, and it can be said from this that a molecular weight is comparatively small and the distribution is sharp. Since it was freed from the way of thinking of carrying out size enlargement and the technique of being size enlargement *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne, previously of forming a back high softening point is adopted after the conventional high-softening-point-izing in this invention, Since hot heat-treatment (thermal polymerization) which it says is required not less than 350 \*\* in manufacture of the conventional high softening point pitch through the 1st process of this invention and the 2nd process, or the polymerization reaction by a catalyst is not used at all, an isotropic high softening point pitch can be economically obtained on a whole surface optical target easily. In the meaning of the isotropic pitch which softening temperature is remarkably high, and a molecular weight is small, and does not contain BTX solvent insoluble matter. It can say that the pitch itself obtained at the 2nd process is very unique, and this characteristic is considered to be a major factor which uniform micro pore generates drastically easily at a next process.

[0033](The 3rd process) It is a process of obtaining the non-deliquesce thing filler by which non-deliquesce was carried out to such an extent that the 3rd process of this invention heats this high softening point pitch by which size enlargement was carried out under the atmosphere containing oxygen, oxidizes and does not cause melting and weld with subsequent heating at least.

[0034]Although the high softening point pitch which is obtained at the 2nd process of this invention and by which size enlargement was carried out does not contain BTX solvent insoluble matter primarily, If this is gradually heated in the atmosphere, for example, air, containing oxygen, the weight increment by oxidation reaction will come to be observed from about 140-160 \*\*, and an ingredient insoluble to a BTX solvent and an ingredient insoluble to quinoline will generate with it. Even if a BTX solvent insoluble element will be 100 % of the weight at this time, in the process accompanied by next heating, melting of a pitch and weld occur, a shape change may be caused or that from which quinoline insoluble is not 100% of the weight yet may interfere with generation of a stoma. The point that the shape change or weld by melting will not take place in a next carbonization process according to this invention person's etc. knowledge. The minimum

requirement required for non-deliquesce [ for the point that the quinoline insoluble in a non-deliquesce thing reaches to 100% of the weight being mostly in agreement, namely, causing neither melting nor weld ] is mostly equivalent to this point, and this point becomes the highest [ the yield after carbonization ] (this non-deliquesce condition is henceforth called optimal non-deliquesce conditions).

[0035]Therefore, in the 3rd process, BTX solvent insoluble matter and quinoline insoluble should just process on conditions severer than the conditions which reach to 100% of the weight substantially, i.e., the optimal non-deliquesce conditions. Especially if the non-deliquesce method can be heated under the atmosphere containing oxygen and oxygen can be made to incorporate, will not be limited, but, Naturally a processing condition changes with oxygen densities in atmosphere, for example, in under an air atmosphere, the heating rate of 0.1-10 \*\* / min, the retention temperature of 250-400 \*\*, and about retention time 0.1-10 hour are adopted.

[0036]If it processes with the above conditions, the particles, the powder, or the fibrous non-deliquesce thing filler by which non-deliquesce was carried out can be obtained to such an extent that melting and weld are not caused with next heating.

[0037]In using particles, powder, or textiles as a porous carbon material as it is, without considering it as the molding body which is an object of this invention, The non-deliquesce thing obtained at this 3rd process is calcinated under the same conditions as the 7th process mentioned later as it is. Although what is necessary is to calcinate and just to carbonize, after performing fault non-deliquesce processing which is carbonized or is mentioned later and considering it as a fault non-deliquesce thing, it cannot be overemphasized that it is also possible to use the fault non-deliquesce thing and carbide which performed these processings as a filler of this invention. However, since there will be no big difference in the generation situation of a stoma if a molding body is changed into a fault non-deliquesce state at the 6th process when a non-deliquesce thing is used, or when a fault non-deliquesce thing or carbide is used, it is advantageous to use a non-deliquesce thing in energy cost.

[0038](The 4th process) The 4th process of this invention uses as a binder the high softening point pitch produced by this non-deliquesce thing filler by making it the same with to the 2nd process of this invention, It is the process of blending so that the quantity of the high softening point pitch to the mixed gross weight of a non-deliquesce thing filler and a high softening point pitch may be 20 to 70 % of the weight, and obtaining a molding material.

[0039]The method of combination mixes a high softening point pitch to a non-deliquesce thing filler, adds a BTX solvent into this mixture, and dissolves a high softening point pitch in it. How to remove and dry a BTX solvent from the mixture containing this solvent after kneading, Or it is preferred to carry out by the method of removing and drying a BTX solvent from the mixture which adds and kneads what dissolved the high softening point pitch in the BTX solvent beforehand, and was used as the solution to a non-deliquesce thing filler, and contains this solvent.

[0040]Although a non-deliquesce thing filler and a high softening point pitch are also mixable by dry type, Since [ to which a path says both as 100micro or less / detailed ] it is powdered, when it is difficult for the circumference of a filler to make a binder adhere enough and mixing is uneven, since the nonuniformity of a molding body may arise and a crack and modification may occur with subsequent heating, sufficient cautions are required. On the other hand, if a high softening point pitch is dissolved and it mixes using a BTX solvent, mixing is very easy and the molding material in which the high softening point pitch which is a binder adhered to the circumference of the non-deliquesce thing filler can be easily obtained by drying this and removing a BTX solvent.

[0041]Each equipment for the dissolution of the high softening point pitch by a BTX solvent, mixing of a filler and a binder, removal of a BTX solvent, and desiccation should just adopt a commercial mixer, a dryer, etc., and special equipment or device are not required.

[0042]The quantity of the BTX solvent added in order to dissolve a high softening point pitch has 0.3 to 10 preferred weight section to high softening point pitch 1 weight section. If there are few BTX solvents than this quantity, the viscosity of the BTX solvent solution of a high softening point pitch becomes high, the big mechanical power at the time of mixing may be required, or it



may become uneven mixing it. On the contrary, even if there are too many BTX solvents, since mixing becomes uneven since a filler will be in the state where it sedimented in the binder solution, and a lot of thermal energies at the time of removal of a BTX solvent and desiccation are needed, it is not desirable.

[0043]the quantity of the high softening point pitch blended with a non-deliquesce thing filler -- 20- of the mixed gross weight of a non-deliquesce thing filler and a high softening point pitch -- it is 30 to 60 % of the weight preferably 70% of the weight. Since the intensity after molding and non-deliquesce, and carbonization will become low if there are few loadings of a high softening point pitch than 20 % of the weight, problems, such as destruction at the time of handling, may arise, and it is not desirable. On the contrary, since melting and that expand and a molding body changes have an inside at the time of non-deliquesce [ of a molding body ] when there are more loadings of a high softening point pitch than 70 % of the weight, it is not desirable too.

[0044]Although a massive portion is sometimes further made [ the loadings of a high softening point pitch, the amount of the BTX solvent used, and ] to a mixture in part according to the kind of mixing, a kneading machine, and dryer, etc., Since these may become the filling operation to the metallic mold at the time of molding, and a homogeneous obstacle of packing, it is preferred to grind and crack these massive portions before molding.

[0045](The 5th process) The 5th process of this invention molds the molding material obtained at the 4th process, and a path or thickness is the process of obtaining molding bodies, such as a pellet type of 10 mm or less, a grain, or tabular. The method of drying, after coming adding the application-of-pressure molding method or a BTX solvent, or extrusion molding can be used for the method of molding.

[0046]When based on application-of-pressure molding, since a binder adheres to the circumference of a filler, the molding material obtained at the 4th process of this invention can be easily used as a molding body by pressurizing as it is. The method of molding should just adopt the method usually known, for example, a path pays the molding material of the specified quantity to a metallic mold of 10 mm or less, and the method of pressurizing by the piston or punch is adopted. Although the molding pressure power at this time is  $0.1\text{--}several\text{ton}/\text{cm}^2$  grade, since the binder has adhered to the circumference of a filler enough, so big a pressure is not needed but below  $1.0\text{ t}/\text{cm}^2$  is enough as it. Near ordinary temperature may be sufficient as the temperature at the time of molding. Although it can also heat, since the softening temperature of a binder is not less than  $180^\circ\text{C}$ , a binder cannot be made to mobilize at a temperature lower than this softening temperature, and it is almost ineffective.

[0047]It is also possible to obtain granular material by a granulation method without using a metallic mold. Since it is meltable to a BTX solvent in the high softening point pitch which is a binder in the case of this invention, A BTX solvent can be used as a fluid for granulations, for example, a non-deliquesce thing filler and a high softening point pitch are put into a rotation bread type granulator, and it can granulate by the method of adding a BTX solvent gradually, rotating this. When a high softening point pitch dries the granular material obtained by acting as a binder for granulations during granulation operation and removes a BTX solvent by this method, as a binder of granular material further. In order to act as a binder at the time of non-deliquesce and carbonization, it is not necessary to use another binder for granulations in particular. It is also possible to add a BTX solvent to a non-deliquesce thing filler and a high softening point pitch, to consider it as paste state, and to mold by the extrusion molding method. In the case of the granulation method molded using these BTXs solvent, or the extrusion molding method, the 4th process and the 5th process of this invention can also be performed simultaneously.

[0048]The shortest distance from the central part of the path or thickness of a molding body obtained at this 5th process being 10 mm or less, i.e., a molding body, to an outside surface needs to be 5 mm or less. Unless non-deliquesce [ to the inside of a molding body ] will become difficult in the non-deliquesce process of the following molding body if the path or thickness of a molding body is larger than this, and non-deliquesce [ of the inside ] is carried out enough, since melting and modification take place at the time of carbonization, or the portion which a stoma

does not generate remains in an inside and it becomes a molding body with an uneven stoma, it is not desirable. The size and intensity of particles of these granular material can be adjusted by choosing the loadings of the high softening point pitch to be used, and the amount of the BTX solvent used.

[0049](The 6th process) The 6th process of this invention carries out non-deliquesce processing of the molding body obtained at the 5th process in the atmosphere containing oxygen, and is a non-deliquesce state and a process preferably changed into a fault non-deliquesce state in both a filler portion and a binder portion.

[0050]It is said that the conditions to which the BTX solvent insoluble matter and quinoline insoluble in a non-deliquesce thing reach to 100% of the weight substantially of the non-deliquesce conditions of the pitch based carbon fiber manufactured paying attention to intensity, i.e., the optimal non-deliquesce conditions indicated at the 3rd process, are generally preferred.

However, if the non-deliquesce thing by the optimal non-deliquesce conditions is carbonized at the 7th following process in the case of this invention, the carbide which has the specific surface area in a temperature requirement as narrow as  $600\text{--}800^\circ\text{C}$  whose carbonization temperature is to some extent big will be obtained, but. When carbonization temperature is lower than this, or in being conversely high, the specific surface area of the carbide obtained becomes small rapidly.

On the other hand, when it processes by a severe condition rather than the optimal non-deliquesce conditions, on the optimal non-deliquesce conditions, there is still an oxygen density in a non-deliquesce thing in the middle of an increase, but. If it adopts and carries out fault non-deliquesce [ of the hot and prolonged conditions ] rather than the optimal non-deliquesce conditions, although the yield of a non-deliquesce thing will fall gradually, above a certain condition, the oxygen density in a non-deliquesce thing becomes almost fixed. When the fault non-deliquesce thing in the state where this oxygen density was saturated is carbonized, while  $500^\circ\text{C}$  as mentioned above the incorporated oxygen  $***$ , many stomata generate, carbide comes to have sufficiently big specific surface area, and this specific surface area comes to be maintained to the elevated temperature of  $1,100^\circ\text{C}$ .

[0051]Therefore, in order to obtain the molding body which has sufficiently big specific surface area in a wide carbonization temperature requirement, it is severer than BTX solvent insoluble matter and quinoline insoluble reach to 100% of the weight substantially in this 6th process rather than only carrying out non-deliquesce on the optimal non-deliquesce conditions. And it is preferred to process on condition of more than with which the oxygen density in this treatment object is saturated, and to change both a filler portion and a binder portion into a fault non-deliquesce state.

[0052]The almost same range as the conditions adopted when this non-deliquesce method in particular is not limited and the size enlargement object of a high softening point pitch is operationally used as a non-deliquesce thing in the 3rd process of this invention. That is, in order to adopt the heating rate of  $0.1\text{--}10^\circ\text{C}/\text{min}$ , the retention temperature of  $250\text{--}400^\circ\text{C}$ , and about retention time  $0.1\text{--}10$  hour under an air atmosphere and to change into a fault non-deliquesce state in this case, it can carry out by adjusting retention temperature and retention time.

[0053]Only the area in which the specific surface area of the non-deliquesce thing pass the 6th process of this invention, or a fault non-deliquesce thing molding body is equivalent to particles, powder, or the outside-surface product of textiles regardless of a processing condition is observed. This shows that the stoma is not necessarily generating in this non-deliquesce stage. [0054](The 7th process) The 7th process of this invention is a process which calcinates the molding body by which non-deliquesce was carried out in an inert atmosphere, and is carbonized at the 6th process.

[0055]Although the usual method of heating a carbonization method in an inert atmosphere may be used, carbonization temperature changes with non-deliquesce conditions in the 6th process as aforementioned. As for the carbonization temperature at the time of fully carrying out fault non-deliquesce [ of the carbonization temperature at the time of carrying out non-deliquesce on the optimal non-deliquesce conditions ] above  $600\text{--}800^\circ\text{C}$  and the optimal non-deliquesce condition, the range of  $500\text{--}1,100^\circ\text{C}$  is chosen. By the method of this invention, the big specific

surface area at the time of this temperature requirement, i.e., a lot of micropores, is obtained.

[0056]The molding body of the fault non-deliquesce thing pass the 1-6th processes by using a naphtha-cracking byproduct oil as a starting material. For example, the inside of a nitrogen atmosphere, if the BET method specific surface area by the nitrogen absorption in liquid nitrogen temperature is measured about what was carbonized by the method of carrying out temperature up by 10 \*\* / min, and holding with prescribed temperature for 1 hour, Although only small specific surface area is observed at the carbonization temperature of 400 \*\*, if [ make only 100 \*\* of temperature high, and ] 500 \*\*, very big specific surface area will come to be observed. Although too big specific surface area is observed at the carbonization temperature of 1,100 \*\*, if it carbonizes at 1,200 \*\* high only 100 more \*\*, only small specific surface area will be observed. Even when the non-deliquesce thing in which the oxygen density is not saturated is carbonized, in the range of 600-800 \*\* carbonization temperature, big specific surface area is observed similarly. That is, by the method of this invention, generation of a stoma and disappearance are very drastic and specific surface area changes a lot by slight change of carbonization conditions. This is considered to be what proves that the stoma in the porous carbon molding body of this invention is very uniform.

[0057]Generation of the stoma as used in the field of this invention and disappearance judge whether adsorption of nitrogen takes place with liquid nitrogen temperature, and do not deny existence of the very detailed stoma which cannot enter nitrogen molecules. For example, a drastic change of the specific surface area by the above-mentioned carbonization temperature, When 1,200 \*\* of carbonization temperature is made high from 1,100 \*\*, most "stomata which can enter nitrogen molecules" which existed at 1,100 \*\* can also be interpreted as their being the results of changing at once at "the very detailed stoma which cannot enter nitrogen molecules."

[0058]Other conditions other than the carbonization temperature in the 7th process of this invention, i.e., a heating rate, retention time, etc. are enough in the range usually used. However, since ranges realizable according to the form of the carbonization furnace which uses a heating rate differ as generally known, In using the carbonization furnace of a batch type, when 1 \*\* / min - 100 \*\* / min grade use the carbonization furnace of continuous system again, the heating rate of 10 \*\* / min - 1,000 \*\* / min grade is adopted, and as for retention time, 1 minute - about 10 hours are adopted.

[0059]The BET method specific surface area according [ the porous carbon molding body obtained by the method of this invention ] to the nitrogen absorption under liquid nitrogen temperature is more than 300-m<sup>2</sup>/g, and the most is concentrating the pole diameter analyzed by the HK method (the Horvath-Kawazoe method) from the adsorption isotherm of nitrogen on 10A or less.

[0060]The method of still measuring a pole diameter, pore distribution, and pore volume correctly about the stoma of detailed molecular size like the stoma generated by the method of this invention is not established, but the value changes fairly a lot with the method of measurement, the technique of analysis, etc. in many cases. Therefore, although the evaluation of the stoma of a molecular size level should evaluate the practical use characteristic for every use, it is usually nitrogen (molecular size, major-axis = 4.1A, a minor axis = 3.0 A) actually. The method of evaluating a stoma in accordance with a specific analytic method from adsorption property, such as a value indicated to JP 4-13288A, is adopted, and when getting to know change of the basic characteristic of material, or the basic characteristic by the manufacturing method or conditions, etc., it is thought that such a valuation method is enough.

[0061]If an above method and conditions are adopted and the method of this invention is enforced, the porous carbon molding body which comprises homogeneous carbon and has uniform micropore can be manufactured efficiently easily.

[0062]According to the method of this invention, it is possible to also manufacture the carbon material in which a stoma does not exist at all, or its molding body, and it can also be said in this meaning that this invention is what provides the one "porosity controlling method" for controlling generation of uniform micropore intentionally.

[0063]

[Example]Hereafter, although a reference example, an example, and a comparative example explain this invention still in detail, the range of this invention is not limited by these examples. Especially % in a reference example, an example, and a comparative example shows weight %, as long as there is no specification.

[0064]When cracking reference example 1 naphtha and manufacturing olefins, distillation under reduced pressure of the heavy oil (naphtha-cracking byproduct oil) which carries out a byproduct was carried out, and the low softening point pitch of 71 \*\* of temperature gradient method softening temperatures was obtained. The yield to the naphtha-cracking byproduct oil of this thing was 73%, 17.9% of the loss on heating up to 300 \*\* and the ultimate analysis value which measured the description of this pitch with 0% of xylene insoluble matter, 0% of quinoline insoluble, and a thermobalance were the H/C atomic ratio 0.90 C92.9%, H7.0%, and S0.02%.

[0065]This pitch is put into the melt spinning machine equipped with a nozzle the diameter (D) of 0.25 mm, and 0.75 mm (L) (L/D ratio=3) in length, It breathed out by discharge-pressure 5 kg/cm<sup>2</sup>, and [ the spinning temperature of 135 \*\*, and ] G, and took over in the air soccer installed in the nozzle lower part, and low softening point pitch textiles with a fiber diameter of 20 micro were obtained.

[0066]Next, 200 g of these low softening point pitch textiles were put in acetone and 4,000 ml of partially aromatic solvents (acetone / SBA capacity factor = 20/80) of SBA, and it agitated with the magnetic stirrer for 1 hour. Then, the insoluble matter which filtered this mixture with the G-4 glass filter, and was obtained except for solvent extractives was again put in 4,000 ml of new partially aromatic solvents, and was agitated for 1 hour. After it filtered this with the same glass filter and methanol washed 3 times, the solid was put into the reduced-pressure-drying machine, it dried at 30 \*\* for 5 hours, and the high softening point pitch which removed the more volatile component was obtained.

[0067]The yield of the obtained high softening point pitch is 58% to low softening point pitch textiles, The description was 216 \*\* of temperature gradient method softening temperatures, 0% of xylene insoluble matter, 0% of quinoline insoluble, and 2.1% of the loss on heating up to 300 \*\*, and the ultimate analysis value was the H/C atomic ratio 0.91 C92.8%, H7.1%, and S0.03%.

although the fiber diameter is almost the same as extraction before when this thing is observed with a scanning electron microscope (SEM) — length — several — it was the fibrous powder cut by 10 mu.

[0068]Subsequently, the powder of these high softening point pitch textiles is heated by the heating rate of 0.5 \*\* / min among the air, Non-deliquesce processing was carried out by \*\* held with the prescribed temperature of 195-355 \*\* for 1 hour, this non-deliquesce thing was further heated by the heating rate of 10 \*\* / min among the nitrogen air current, and it carbonized by holding at 1,000 \*\* for 1 hour. The yield of a non-deliquesce thing, description, and the yield and appearance of carbide are shown in Table 1. Yield was based on the high softening point pitch textiles after more volatile component extraction.

[0069]Since fuse by a thing with a non-deliquesce temperature of 215 \*\* or less from Table 1 at the time of carbonization, and textiles shape cannot be maintained, and the textiles of what has stopped textiles shape cause weld in the case of 235 \*\* non-deliquesce temperature and it becomes massive, The minimum non-deliquesce temperature that can be carbonized without textiles welding is 255 \*\*, and in aiming at textiles intensity, it turns out that this condition turns into the optimal non-deliquesce conditions.

[0070]If the property variation of a non-deliquesce thing is seen, quinoline insoluble will have reached to 100% exactly at the time of the optimal non-deliquesce conditions, but it turns out that there is still an oxygen density in the middle of an increase, and it increases to the non-deliquesce temperature of about 300 \*\*, and is mostly saturated above 300 \*\*.

[0071]Next — the obtained carbide — a direct reading type surface area measuring device and MONOSORB (MS-8 type.) In accordance with the ASTM method (Draft Proposal 7-18-76, Revision 2.4-6-81), BET method specific surface area (SA (BET)) was measured from the amount of nitrogen absorption at liquid nitrogen temperature using the product made by

QUANTACHROME. The result is also shown in Table 1. From the table, only very small specific surface area is observed on the optimal non-deliquesce conditions (255 \*\*, and 355 \*\*). Above that which made non-deliquesce temperature high and was changed into the fault non-deliquesce state, i.e., the condition with which the oxygen density in a non-deliquesce thing is saturated mostly, (295 \*\*), although the stoma that nitrogen adsorbs hardly exists, it turns out that big specific surface area is observed and the detailed stoma is generating.

[0072]The adsorption isotherm in liquid nitrogen temperature was measured using the adsorption isotherm measuring device BELSORP-28SA type (product made from Japanese Bell) about the carbide obtained at the non-deliquesce temperature of 255 \*\*, and 355 \*\*, and the specific surface area (SA (Lang)) by the Langmuir method was determined from this data. The result is shown according to Table 1. The specific surface area determined from adsorption isotherm is below 1-m<sup>2</sup>/g too at the non-deliquesce temperature of 255 \*\*, and not generating the stoma that nitrogen adsorbs was reconfirmed. The big value 688m<sup>2</sup>/g was checked in the thing with a non-deliquesce temperature of 355 \*\*.

[0073]It is well-known it to be large to the value from which the difference in the theoretical calculation equation used when it is specific surface area measurement of a detailed stoma, and performing the difference in a measuring method and calculation of specific surface area is obtained, although the BET adsorption method for which the value of the specific surface area by these Langmuir methods used MONOSORB became a different value, and to influence. Although it was judged by verifying the effect of this invention that which method could be used, in the example, it mainly measured with the BET adsorption method, and measured by the Langmuir method selectively.

[0074]The specific surface area of the non-deliquesce thing before carrying out the above carbonization treatment is a 0.2-0.4-m<sup>2</sup>/g grade, also when which non-deliquesce conditions are adopted.

This was a value almost equivalent to a fiber diameter and the outside-surface product calculated from length.

Therefore, it is thought at the non-deliquesce time that the stoma was not generated.

[0075]The adsorption desorption constant temperature line of nitrogen at the liquid nitrogen temperature of the carbide which acquired non-deliquesce temperature as 355 \*\* is shown in drawing 1. It turns out that almost all adsorption has taken place from the figure in the field where relative pressure (P/P<sub>s</sub>, adsorption-equilibrium pressure of nitrogen at P<sub>s</sub> measurement temperature, P<sub>s</sub>: maximum vapor tension of nitrogen at measurement temperature) is very small, i.e., the sharp very detailed stoma of distribution exists in the carbide. In drawing 1, some hysteresis is observed in the constant temperature line at the time of adsorption (it is round), and the constant temperature line at the time of desorption (point). Although such a hysteresis is often observed in measurement of a very detailed stoma and is not clarified about the cause, this does not deny generation of uniform micropore.

[0076]When pore distribution was calculated in accordance with the HK method (the Horvath-Kawazoe method) from this data, it was checked that a main pole diameter is about 6Å, and the stoma of this carbon material is the uniform micropore which carried out sharp distribution.

[0077]  
[Table 1]

表 1

不融化温度 ℃	不融化物の収率と性状				炭化物の収率と性状			
	収率 wt%	不溶分 wt%	元素分析値 wt%		収率 wt%	外觀	比表面積 m <sup>2</sup> /g	
			1/15	C	H	O	SA (BET)	SA (Lang)
185	103	69	0	86.7	6.2	7.1	—	—
215	103	100	33	—	—	—	—	—
235	102	100	75	78.4	4.5	17.1	63	—
255	100	100	100	—	—	—	64	0.2
275	96	100	100	71.2	3.1	26.7	60	0.3
295	91	—	—	—	—	—	68	0.6
315	90	—	—	80.5	2.3	28.2	320	—
335	82	—	—	—	—	—	868	—
355	77	—	—	69.5	2.0	20.5	882	—
							877	688

[0078]The fibrous powder of the high softening point pitch which acquired non-deliquesce temperature by solvent extraction by the reference example 1 as well as the non-deliquesce thing obtained as 355 \*\* by the example 1 reference example 1. The quantity of the high softening point pitch to the mixed gross weight of a non-deliquesce thing and a high softening point pitch was mixed so that it might become 0, 20, 30, 40, 60, 80, and 100%, and it was 10 g in total quantity. After added 6 ml of xylene to this, dissolved the high softening point pitch, having kneaded, after mixing enough, having ranked second, carrying out reduced pressure drying at 60 \*\* and removing xylene from a mixture, the mortar ground lightly and the whole quantity obtained the molding material of 35 or less meshes.

[0079]This molding material was molded by the pelletizer (Okada elaborate N-30 Type) provided with the metallic mold with a diameter of 3 mm, and the molding body of the diameter of 3 mm and about 3 mm in length a cylindrical pellet was obtained.

[0080]Subsequently, temperature up of this molding body was carried out to 355 \*\* by the heating rate of 0.5 \*\* / min among the air, and it carried out non-deliquesce by holding at this temperature for 1 hour. This non-deliquesce condition is conditions from which a high softening point pitch incorporates oxygen enough, and will be in a fault non-deliquesce state so that clearly from the reference example 1.

[0081]Next, temperature up of the fault non-deliquesce thing of this molding body was carried out by the heating rate of 10 \*\* / min among the nitrogen air current, and it carbonized by holding at 1,000 \*\* for 1 hour. The BET method specific surface area (SA (BET)) measured like the appearance of the obtained carbide, yield, and the reference example 1 is shown in Table 2. [0082]The table shows that the inside fused and blistered at not less than 80% at the time of non-deliquesce, and the compounding ratio of that it cannot be molded and a high softening point pitch was not able to maintain shape of the molding body in a non-deliquesce thing independent, and that the value of specific surface area becomes remarkably small by the thing which internal melting generated. In the case of the carbide obtained in the range whose compounding ratio of a high softening point pitch is 20 to 60%, it turns out that big specific surface area is obtained like the reference example 1.

[0083]  
[Table 2]

表 2

配合比 (wt%)	成型体に対する 炭化物の収率 (wt%)		炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
	高炭化点 <sup>1)</sup>	低炭化点 <sup>2)</sup>		
100	0	0	—	—
80	20	0	良好	39.6
70	30	0	良好	38.6
60	40	0	良好	39.0
40	60	0	良好	38.9
20	80	0	不炭化時に膨れ	1.2
0	100	0	不炭化時に膨れ	—

[0084]Non-deliquesce [ of the molding body whose compounding ratio of the high softening point pitch obtained in comparative example 1 Example 1 is 20 to 60% ] was not carried out, but it was carbonized on the conditions same as it is as Example 1, and carbide was obtained. The BET method specific surface area (SA (BET)) measured like the appearance of the obtained carbide, yield, and the reference example 1 is shown in Table 3.

[0085]The table shows that the specific surface area of the carbide at the time of not carrying out non-deliquesce after molding serves as a remarkable small value.

[0086]

[Table 3]

表 3

配合比 (wt%)	成型体に対する 炭化物の収率 (wt%)		炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
	高炭化点 <sup>1)</sup>	低炭化点 <sup>2)</sup>		
80	20	40	良好	0.2
60	40	40	やや膨れ、膨脹	0.2
40	60	39	膨脹、形状崩れ	1.1

[0087]Except using n-pentanol as an extraction solvent, it extracted, swabbed in methanol and dried by the same method as the reference example 1, and the fibrous powder of the high softening point pitch was obtained from low softening point pitch textiles with a diameter of 20 micro obtained by the reference example 2 reference example 1. The yield of this thing was 51% to low softening point pitch textiles, that description was 232 \*\* of temperature gradient method softening temperatures, 0% of xylene insoluble matter, 0% of quinoline insoluble, and 1.8% of the loss on heating up to 300 \*\*, and the ultimate analysis value was the H/C atomic ratio 0.91 C92.8%, H7.1%, and S0.02%.

[0088]Subsequently, the fibrous powder of this high softening point pitch is heated by the heating rate of 0.5 \*\* / min among the air. By holding for 1 hour with the prescribed temperature of 255 \*\*, 305 \*\*, 355 \*\*, and 395 \*\*, non-deliquesce processing was carried out, this non-deliquesce thing was further heated by the heating rate of 10 \*\* / min among the nitrogen air current, and it carbonized by holding at 1,000 \*\* for 1 hour. The yield of a non-deliquesce thing, description, and the yield and description of carbide are shown in Table 4. About the specific surface area of the obtained carbide, BET method specific surface area (SA (BET)) and the Langmuir method specific surface area (SA (Lang)) were measured like the reference example 1. [0089]If what made non-deliquesce temperature 255 \*\* is carbonized at 1,000 \*\*, specific surface area will be small and most generation of a stoma will not be accepted, but in what made non-deliquesce temperature high with 305 \*\*, 355 \*\*, and 395 \*\*, it turns out that big specific surface area is observed and the detailed stoma is generating.

[0090]If almost all adsorption has taken place in the low place of relative pressure (P/Ps) and pore distribution is calculated by the HK method from the data like drawing 1, the non-deliquesce temperature of 305 \*\*, and 355 \*\* adsorption isotherm, it was checked that all are the stomata which carried out sharp distribution which has the center of a pole diameter in about 6 A.

[0091]

[Table 4]

表 4

不炭化温度 ℃	不炭化物の収率と性状				炭化物の収率と性状			
	収率 wt%	不溶分 wt%	元素分析値 wt%		収率 wt%	外観	比表面積 m <sup>2</sup> /g	
			C	H			SA (BET)	SA (Lang)
255	103	100	100	—	61	良好	0.2	0.5
305	93	—	68.2	2.2	51	良好	37.1	58.9
355	77	—	67.7	2.0	30.3	良好	38.6	63.8
395	38	—	—	—	17	良好	39.8	—

[0092]The high softening point pitch of 3 g which acquired non-deliquesce temperature by the reference example 2 as well as the non-deliquesce thing 7g obtained as 355 \*\* was mixed by the example 2 reference example 2, 3 ml of xylene was added to this, and the high softening point pitch was dissolved and kneaded. After reduced pressure drying and a mortar ground this at 60 \*\* like Example 1, and the powdered molding material of 35 or less meshes was obtained. This thing was molded by the same pelletizer as Example 1, and the molding body of the diameter of 3 mm and about 3 mm in length a cylindrical pellet was obtained.

[0093]Subsequently, by carrying out temperature up of this molding body by the heating rate of 0.5 \*\* / min among the air, and holding with the prescribed temperature of 255 \*\*, 305 \*\*, and 355 \*\* for 1 hour, non-deliquesce was carried out, this molding body by which non-deliquesce was carried out was carbonized at the carbonization temperature of 1,000 \*\* like Example 1, and carbide was obtained. The BET method specific surface area (SA (BET)) measured like the appearance of the obtained carbide, yield, and the reference example 1 is shown in Table 5.

[0094]When what made non-deliquesce temperature of the molding body 255 \*\* was carbonized at 1,000 \*\* from the table and it changes into that the specific surface area as the whole molding body becomes small, and a fault non-deliquesce state, it turns out that the specific surface area becomes almost equivalent to the specific surface area in the end of fibrous carbon powder shown in the reference example 2. It was 650m<sup>2</sup>/g when the specific surface area (SA (Lang)) by the Langmuir method was measured like the reference example 1 about the carbide obtained at the non-deliquesce temperature of 355 \*\*.

[0095]The adsorption desorption constant temperature line of nitrogen at the liquid nitrogen temperature of the carbide is shown in drawing 2. It turns out that almost all adsorption of the obtained molding body has taken place from the figure in the field where relative pressure (P/Ps) is very small, i.e., the sharp very detailed stoma of distribution is generating. It turns out that drawing 2 shows the almost same adsorption desorption constant temperature line as drawing 1 of the reference example 1, and the almost same stoma is generating also in the case of the molding body obtained from this in accordance with the method of powdered voice or this invention. When pore distribution was calculated by the HK method like the reference example 1 from this data, it was checked that it is the stoma which carried out sharp distribution which has the center of a pole diameter in about 6 A.

[0096]

[Table 5]

表 5

成型体の不炭化温度 (℃)	成型体に対する 炭化物の収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
255	40	良好	26.4
305	48	良好	36.3
355	38	良好	38.6

[0097]The high softening point pitch of 3 g which acquired non-deliquesce temperature by the reference example 2 as well as the non-deliquesce thing 7g obtained as 255 \*\* was mixed by the example 3 reference example 2, 3 ml of xylene was added to this, and the high softening point pitch was dissolved and kneaded. After reduced pressure drying and a mortar ground this at 60 \*\* like Example 1, and the powdered molding material of 35 or less meshes was obtained. It molded by the same pelletizer as Example 1, and the molding body of the diameter of 3 mm and about 3 mm in length a cylindrical pellet was obtained. Subsequently, by carrying out temperature up of this molding body by the heating rate of 0.5 \*\* / min among the air, and holding at 355 \*\* for 1 hour, non-deliquesce was carried out, this molding body by which non-deliquesce was carried out was carbonized at 1,000 \*\* like Example 1, and carbide was obtained. The appearance of the obtained carbide was good and, as for the carbide yield to a molding body, 393m<sup>2</sup>/g and the Langmuir method specific surface area (SA (Lang)) of BET method specific surface area (SA (BET)) were 688m<sup>2</sup>/g 39%.

[0098]The adsorption desorption constant temperature line of nitrogen at the liquid nitrogen temperature of the carbide is shown in drawing 3. It turns out that almost all adsorption of the obtained molding body has taken place from the figure in the field where relative pressure (P/P<sub>s</sub>) is very small, i.e., the sharp very detailed stoma of distribution is generating. It turns out that drawing 3 shows drawing 1 of the reference example 1, and the almost same adsorption desorption constant temperature line as drawing 2 of Example 2, and the sharp micropore of distribution is generating from this to the carbide.

[0099]When pore distribution was calculated by the HK method like the reference example 1 from this data, it was checked that it is the stoma which carried out sharp distribution which has the center of a pole diameter in about 6 Å.

[0100]The fibrous powder of the high softening point pitch obtained by solvent extraction by the reference example 1 as well as the fault non-deliquesce thing which acquired non-deliquesce temperature as 355 \*\* by the example 4 reference example 1 was added by the predetermined ratio, and the total quantity was 10 g. After mixing enough, 6 ml of xylene was added to this, and the high softening point pitch was dissolved and kneaded. Subsequently, after carrying out reduced pressure drying at 60 \*\* and removing xylene from a mixture, the mortar ground lightly and the whole quantity obtained the molding material of 60 or less meshes. This molding material was molded by 133 kg of the total load using a metallic mold 6 mm in inside diameter, and the molding body of the diameter of 6 mm and about 6 mm in length a cylindrical pellet was obtained. Subsequently, temperature up of this molding body was carried out to 355 \*\* by the heating rate of 0.5 \*\* / min among the air, and it carried out non-deliquesce by holding at this temperature for 1 hour. This non-deliquesce condition is conditions from which a high softening point pitch incorporates oxygen enough, and will be in a fault non-deliquesce state so that clearly from the reference example 1.

[0101]Next, temperature up of the fault non-deliquesce thing of this molding body was carried out by the heating rate of 10 \*\* / min among the nitrogen air current, and it carbonized by holding at 1,000 \*\* for 1 hour. The appearance, yield, and BET method specific surface area (SA (BET)) of the obtained carbide are shown in Table 6. It turns out that big specific surface area is obtained by the molding body by application-of-pressure molding as well as Example 1.

[0102]

[Table 6]

表 6

配合比 (wt%)	成型体に対する 炭化物収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
過不炭化物	炭化点 ± 1		
80	20	良好、やや脆い	411
70	30	良好	381
60	40	良好	368
40	60	良好	384

[0103]The high softening point pitch textiles extracted and obtained by n-pentanol by the reference example 3 reference example 2 The inside of the air, By heating to 355 \*\* by the heating rate of 0.5 \*\* / min, and holding at 355 \*\* for 1 hour, non-deliquesce was carried out, this non-deliquesce thing was further heated by the heating rate of 10 \*\* / min among the nitrogen air current, and it carbonized by holding at 400-1,500 \*\* for 1 hour. The ultimate analysis, BET method specific surface area (SA (BET)), and the Langmuir method specific surface area (SA (Lang)) of the obtained carbide are shown in Table 7.

[0104]When the stoma measured by nitrogen absorption is rapidly generated from the time of carbonization temperature exceeding 400 \*\* and 1,100 \*\* is exceeded from the result of the table, it turns out that it disappears rapidly. It was checked from the result of the adsorption isotherm measured with the BELSORP-28SA type that each thing with a carbonization temperature of 600-1,100 \*\* is a porous carbon material with the micropore of the sharp distribution whose central diameter is about 6 Å.

[0105]

[Table 7]

表 7

炭化温度 ℃	元素分析値 (wt%)				比表面積 (m <sup>2</sup> /g)	
	C	H	O	S A (BET)	S A (Lang)	
400	70.2	2.1	27.8	2.2	-	-
600	70.5	2.0	18.4	8.73	-	-
800	90.5	2.0	7.5	8.80	7.53	-
1000	98.5	0.6	2.8	8.80	7.74	-
1100	99.4	0.2	0.1	8.85	8.88	-
1200	99.8	0.1	0.0	9.29	6.53	-
1300	-	-	-	0.8	-	-
1500	-	-	-	0.3	-	-

[0106]The high softening point pitch of 3 g which acquired non-deliquesce temperature by the reference example 2 as well as the non-deliquesce thing 7g obtained as 355 \*\* was mixed by the example 5 reference example 2, 3 ml of xylene was added to this, and the high softening point pitch was dissolved and kneaded. After reduced pressure drying and a mortar ground this at 80 \*\* like Example 1, and the powdered molding material of 35 or less meshes was obtained. This thing was molded by the same pelletizer as Example 1, and the molding body of the diameter of 3 mm and about 3 mm in length a cylindrical pellet was obtained. Subsequently, temperature up of this molding body was carried out by the heating rate of 0.5 \*\* / min among the air, and it carried out non-deliquesce by holding at 355 \*\* for 1 hour. This molding body by which non-deliquesce was carried out was held at a predetermined temperature of 400-1,300 \*\* by the heating rate of 10 \*\* / min among the nitrogen air current for 1 hour, and carbide was obtained. The appearance, yield, and BET method specific surface area (SA (BET)) of the obtained carbide are shown in Table 8.

[0107]When carbonization temperature is lower than the table (400 \*\*), in being too high (1,150 \*\*, 1,300 \*\*), specific surface area should become small. And it turns out that the specific surface area of the carbide in which carbonization temperature was acquired at 600 and 800 or 1,000 \*\* will become big almost on a par with the carbide shown by the reference example 3.

[0108]

[Table 8]

表 8

成型体の不融化温度 (°C)	成型体に対する 炭化物収率 (wt%)	炭化後の外観	比表面積 SA(BET) (m <sup>2</sup> /g)
4.00	6.7	良好	8.3
6.00	4.4	良好	4.03
8.00	3.6	良好	4.02
1.000	3.6	良好	3.86
1.150	3.7	良好	1.78
1.300	3.7	良好	2.4

[0109]The same naphtha-cracking byproduct oil as the reference example 4 reference example 1 was distilled, and the low softening point pitch of 49 \*\* of temperature gradient method softening temperatures was obtained. Xylene 30 weight section was added to this low softening point pitch 70 weight section, it dissolved in it, and the solution of the low softening point pitch was prepared, next, a non-ion system surface-active agent (polyoxyethylene nonphenyl ether.) Make into carrier fluid the water containing Kao emulgen 9852%, and a microporous glass with a pore diameter of 4 micro is made into dispersion media using a film emulsification test device (product made from the Ise chemicals). By extruding the solution of the above-mentioned low softening point pitch in carrier fluid through these dispersion media, the low softening point pitch solution prepared under water what is called an O/W type emulsion of which 11 capacity % distribution was done.

[0110]Next, it was dropped gradually, agitating this emulsion in 10-times the amount SBA, and the xylene used for the soluble component in a low softening point pitch and the dissolution was extracted. This mixed liquor was centrifuged, solid content was obtained, and it dried after washing with methanol. This solid content was put in 20-times the amount n-pentanol, and was agitated, it washed and dried with methanol after filtration, and the spherical particle of the high softening point pitch was obtained. The yield to the low softening point pitch of this thing was 48%. The obtained high softening point pitch was 16micro in mean particle diameter, the description was 243 \*\* of temperature gradient method softening temperatures, 0% of xylene insoluble matter, 0% of quinoline insoluble, and 1.7% of the loss on heating up to 300 \*\*, and the ultimate analysis value was the H/C atomic ratio 0.92 C92.7%, H7.1%, and S0.02%.

[0111]Non-deliquesce [ of this thing ] was carried out at 355 \*\* like the reference example 1 for 1 hour, it was carbonized at 1,000 more \*\* for 1 hour, and spherical carbon particles were obtained. The yield at the time of non-deliquesce and carbonization was 72% and 40%, respectively on the basis of the high softening point pitch particles after n-pentanol extraction, and the BET method specific surface area (SA (BET)) of the obtained carbon particle was 375m<sup>2</sup>/g.

[0112]In the non-deliquesce thing 6g of the spherical particle obtained by emulsion-ization by the example 6 reference example 4, the spherical particle 4g of the high softening point pitch similarly obtained by the reference example 4 was mixed, 4 ml of benzene was added to this, and the high softening point pitch was dissolved and kneaded. Then, it ground after reduced pressure drying at 60 \*\* like Example 1, and the molding material of 35 or less meshes was obtained. This thing was molded by the same pelletizer as Example 1, and the molding body of the diameter of 3 mm and about 3 mm in length a cylindrical pellet was obtained.

[0113]Subsequently, by carrying out temperature up of this molding body by the heating rate of 0.5 \*\* / min among the air, and holding at 355 \*\* for 1 hour, non-deliquesce was carried out, it carbonized at 1,000 \*\* like Example 1 further, and carbide was obtained. The appearance of the obtained carbide was good, the carbide yield to a molding body was 39%, and BET method specific surface area (SA (BET)) was 383m<sup>2</sup>/g.

[0114]Non-deliquesce temperature was 355 \*\* by the example 7 reference example 2, the high softening point pitch of 3 g obtained by the reference example 2 as well as the carbide 7g carbonized and obtained at 1,000 \*\* was mixed, 3 ml of xylene was added to this, and the high softening point pitch was dissolved and kneaded. After reduced pressure drying and a mortar

ground this at 60 \*\* like Example 1, and the powdered molding material of 35 or less meshes was obtained. This thing was molded by the same pelletizer as Example 1, and the molding body of the diameter of 3 mm and about 3 mm in length a cylindrical pellet was obtained. Subsequently, by carrying out temperature up of this molding body by the heating rate of 0.5 \*\* / min among the air, and holding at 355 \*\* for 1 hour, non-deliquesce was carried out, it carbonized at 1,000 \*\* like Example 1 further, and carbide was obtained.

[0115]The appearance of the obtained carbide was good and, as for the yield to a molding body, 409m<sup>2</sup>/g and the Langmuir method specific surface area (SA (Lang)) of BET method specific surface area (SA (BET)) were 848m<sup>2</sup>/g 72%. When pore distribution was calculated by the HK method like the reference example 1 from this data, it was checked that it is the stoma which carried out sharp distribution which has the center of a pole diameter in about 6 Å.

[0116]Without carrying out non-deliquesce [ of the molding body of the cylindrical pellet obtained in comparative example 2 Example 7 ], it carbonized on the conditions same as it is as Example 1 1,000, and carbide was obtained. Although the yield to the molding body of carbide was 72% and the shape was good, BET method specific surface area (SA (BET)) was as small as 42-m<sup>2</sup>/g.

[0117]The non-deliquesce thing processed and obtained at the non-deliquesce temperature of 255 \*\* by the reference example 5 reference example 2 was heated by the heating rate of 10 \*\* / min among the nitrogen air current like the reference example 3, and it carbonized by holding with the prescribed temperature of 500-1,000 \*\* for 1 hour. In the carbonization treatment of this non-deliquesce thing, while the exhaust gas which comes out from a carbonization furnace became muddy white from near 300 \*\*, it was observed that dark-brown tarry material adheres to the inside of a work tube outlet part from brown. The yield and BET method specific surface area (SA (BET)) to a fibrous high softening point pitch of the obtained carbide are shown in Table 9. When the non-deliquesce thing in which an oxygen density is not saturated is carbonized from the result of the table, comparatively big specific surface area is observed in a carbonization temperature requirement as narrow as 800-800 \*\*, but at the temperature less than it or beyond it, it turns out that specific surface area is small rapidly.

[0118]

表 9

炭化温度 °C	高軟化点材料に対する炭化物収率 (wt%)	比表面積 SA(BET) (m <sup>2</sup> /g)
500	7.1	5.9
600	6.6	3.28
800	6.3	2.98
800	6.2	1.65
1,000	6.1	0.2

[0119]In the non-deliquesce thing 14g processed and obtained at the non-deliquesce temperature of 255 \*\* by the example 8 reference example 2, the fibrous powder 6g of the high softening point pitch similarly obtained by the reference example 2 was mixed, 6 ml of xylene was added to this, and the high softening point pitch was dissolved and kneaded. After reduced pressure drying and a mortar ground this at 60 \*\* like Example 1, and the powdered molding material of 20 or less meshes was obtained. This thing was molded by the same pelletizer as Example 1, and the molding body of the diameter of 3 mm and about 3 mm in length a cylindrical pellet was obtained. Subsequently, temperature up of this molding body is carried out by the heating rate of 0.5 \*\* / min among the air, By holding at 255 \*\* for 1 hour, non-deliquesce was carried out, temperature up of this non-deliquesce thing was further carried out by the heating rate of 10 \*\* / min among the nitrogen air current, and it carbonized by holding at each temperature of 600 \*\*, 800 \*\*, and 1,000 \*\* for 1 hour.

[0120]The yield and BET method specific surface area to a molding body of the obtained carbide

are shown in Table 10. When the non-deliquesce thing which performs non-deliquesce [ of a filler ] and non-deliquesce [ of a molding body / each of ] at 255 °C and in which an oxygen density is not saturated from the table is carbonized, big specific surface area is observed at the carbonization temperature of 600-800 °C, but at the carbonization temperature of 1,000 °C, it turns out that specific surface area decreases. Therefore, in order to obtain the carbide which has big specific surface area in a wider carbonization temperature requirement, a molding body is understood that it is more desirable to change into a fault non-deliquesce state.

[0121]

[Table 10]

表 10		
炭化温度 ℃	成型体に対する 炭化物収率 (wt%)	比表面積 SA(BET) ( $\text{m}^2/\text{g}$ )
600	62	936
800	59	936
1000	59	77

[0122]

[Effect of the Invention]After using as a starting material the low softening point pitch etc. which are obtained from cheap heavy oil or it and carrying out size enlargement of the heavy oil of a starting material, etc. first according to the method of this invention, in order to adopt the method of attaining high softening point-pitch by solvent extraction. When manufacturing a high softening point pitch conventionally, for example, it had become a problem, a raw material A high price, Economical, in order [ in accordance with hot heat-treatment ] to use the filler and binder which can avoid a technical problem and are obtained from the still more nearly same starting material. By the conventional method, the porous carbon molding body which comprises homogeneous carbon which was not obtained and has uniform micropore can be obtained that it is simple and efficiently industrially. Since the molding body obtained by this invention method has homogeneous and uniform micropore, it is useful as a molecular adsorption agent, a catalyst, electrode carbon, etc.

[Translation done.]

## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

## DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]In the reference example 1, it is an adsorption desorption constant temperature line of nitrogen at the liquid nitrogen temperature of a porous carbon material when non-deliquesce temperature is 355 \*\*.

[Drawing 2]In Example 2, it is an adsorption desorption constant temperature line of nitrogen at the liquid nitrogen temperature of the porous carbon molding body which acquired the non-deliquesce temperature of the 6th process as 355 \*\*.

[Drawing 3]It is an adsorption desorption constant temperature line of nitrogen at the liquid nitrogen temperature of the porous carbon molding body obtained in Example 3.

[Translation done.]